G11608

TEXTBOOKS OF PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., D.Sc., F.R.S.

F. G. DONNAN, C.B.E., M.A., PH.D., F.I.C., F.R.S.

CENTRAL LIBRARY WB

TEXT-BOOKS OF PHYSICAL CHEMISTRY.

Edited by F. G. Donnan, C.B.E., D.Sc., F.R.S.

STOICHIOMETRY. By Sydney Young, D.Sc., F.R.S. With 93 Figures in the Text. 8vo. 12s. 6d. net.

THE PHASE RULE AND ITS APPLICATIONS. By Alex. Findlay, M.A., Ph.D., D.Sc., F.I.C. With 165 Figures in the Text. Crown 8vo. 10s. 6d. net.

SPECTROSCOPY. By E. C. C. Baly, C.B.E. M.Sc., F.R.S. With Illustrations. In Four Volumes. Vol. I. 8vo. 14s. net. Vol. II. 18s. net. Vol. III. 22s. 6d. net.

THERMOCHEMISTRY. By Julius Thomsen. Translated by Katharine A. Burke, B.Sc. (Lond.). Crown 8vo. 12s. 6d. net.

ELECTRO-CHEMISTRY. Part I. General Theory. By R. A Lehfeldt, D.Sc. Including a Chapter on the Relation of Chemical Constitution to Conductivity. By T. S. Moore, B.A., B.Sc. With 55 Figures. Crown 8vo. 7s. 6d. net.

STEREOCHEMISTRY. By Alfred W. Stewart, D.Sc. With 58 Illustrations. 8vo. 12s 6d. net.

METALLOGRAPHY. By Cecil H. Desch, D.Sc., Ph.D., F.I.C., F.C.S., F.R.S. With 14 Plates and 105 Diagrams. Crown 8vo. 16s. net.

THE THEORY OF ALLOTROPY. By A. Smits, Ph.D. Translated by J. Smeath Thomas, D.Sc. With 239 Illustrations. 8vo. 21s. net.

THE EFFECTS OF MOISTURE ON CHEMICAL AND PHYSICAL CHANGES. By J. W. Smith, B.Sc., Ph.D. With 44 Illustrations. 8vo. 15s. net.

PHOTO-PROCESSES IN GASEOUS AND LIQUID SYSTEMS. By R. O. Griffith, D.Sc., and A. McKeown, D.Sc. With 52 Illustrations. 8vo. 25s. net.

A SYSTEM OF PHYSICAL CHEMISTRY. By William C. McC. Lewis, D.Sc. (Liv.), F.R.S. 3 vols. 8vo.
  Vol. I. Kinetic Theory. With 55 Diagrams. 15s. net.
  Vol. II. Thermodynamics. With 55 Diagrams. 15s. net.
  Vol. III. Quantum Theory. With certain Appendices by James Rice, M.A., A. McKeown, M.Sc., and R. O. Griffith, M.Sc. With 12 Diagrams. 15s. net.

LONGMANS, GREEN AND CO. LTD.

LONDON, NEW YORK, TORONTO, CALCUTTA, BOMBAY AND MADRAS.

Syst

Static Equilibrium.
(Treated in "Mechanics".)

Physical Equili
Distribution of
in space. State
Continuity of
gaseous states.
tion of s

Homog
effects
or (
Energy
of

Homogeneous Equilibrium in Gaseous Systems:
(*a*) Reactions involving no change in the number of molecules.
(*b*) Reactions involving change in the number of molecules

Ho
libr
Sys
(
tur
(
tio
sur
dis
tic
mo
(
sol

TABLE INDICATI

M.

ems in Equilibrium.

Dynamic Equilibrium.

brium, i.e.
Molecules
s of matter.
liquid and
Constitu-
olids.

Chemical Equilibrium.

Chemical Equilibrium in Homogeneous Systems, or "*Homogeneous Equilibrium*".

eneous Equilibrium,
lue to Gravitation
xternal) Radiant
being absent. Law
Mass Action.

Homogeneous Equilibrium affected by (external) Radiant Energy. Photochemical "Stationary State".

mogeneous Equi-
ium in Liquid
tems:
i) Liquid mix-
es.
) Dilute solu-
is. (Osmotic pres-
e. Electrolytic
ociation. Osmo-
theory of electro-
tive force.)
) Concentrated
tions.

Homogeneous Equilibrium in Solid Systems: Solid Solutions.

Heterogeneous Equilibrium when effects due to capillarity and radiant energy are absent.

The Distribution Law.

The Phase Law.

A SYSTEM OF
PHYSICAL CHEMISTRY

WILLIAM C. McC. LEWIS, M.A. (R.U.I.), D.Sc. (Liv.), F.R.S.
BRUNNER PROFESSOR OF PHYSICAL CHEMISTRY IN THE
UNIVERSITY OF LIVERPOOL

IN THREE VOLUMES

VOLUME I
KINETIC THEORY

NEW IMPRESSION

LONGMANS, GREEN AND CO. LTD.
39 PATERNOSTER ROW, LONDON, E.C. 4
NEW YORK, TORONTO
CALCUTTA, BOMBAY AND MADRAS
1929

"SCIENCE is nothing without generalisations. . . . The suggestion of a new idea, or the detection of a law, supersedes much that had previously been a burden upon the memory, and by introducing order and coherence facilitates the retention of the remainder in an available form."

LORD RAYLEIGH.

BIBLIOGRAPHICAL NOTE

First Edition. Two Volumes. February, 1916.

The Second Edition was issued in Three Volumes.
Volume I. September, 1918.

New Impressions, March, 1920; June, 1921; April, 1923; July, 1926; and November, 1929.

Made in Great Britain

All rights reserved

PREFACE TO SECOND EDITION.

THE general plan and arrangement followed in the first edition has been adhered to in the present one. A number of changes, however, necessitated by the advances which physical chemistry has made in the last few years, have been introduced, with the result that the book has undergone considerable expansion.

The principal change is the addition of a third volume (in place of a single chapter), in which an account is given of the Quantum Theory in its physico-chemical aspect. The *rôle* which the quantum theory now plays in physical and chemical research makes it imperative for the advanced student to be familiar to some extent with the ramifications of this remarkable concept of energy transfer. The success which has attended the application of this theory, especially in connection with problems which the kinetic theory and thermodynamics by themselves are incapable of solving, constitutes its main claim to consideration. In view of the rather unique character of the quantum theory many of the problems dealt with in Vol. III. do not find a counterpart in Vols. I. and II. There is, however, no real lack of continuity, as the reader will doubtless perceive for himself. Incidentally the addition of a third volume obviates the necessity of division into the three Parts employed in the previous edition.

Among the new additions to Vol. I. may be mentioned: the investigation of crystal structure by means of X Rays, various properties of the colloidal state, recent investigations on the dissociation of ammonium chloride vapour, the Dual Theory of homogeneous catalysis, the Displacement Effect, and Langmuir's theory of heterogeneous reaction velocity, catalysis, and the mechanism of surface effects generally.

In Vol. II. a brief consideration of entropy has been included, more particularly with the object of leading up to Boltzmann's probability-entropy relation in statistical mechanics (which is dealt with in Vol. III.), whereby a statistical basis for the second law of thermodynamics is obtained. The principal change in Vol. II. is the inclusion of a new chapter dealing with the still debatable subject of osmotic pressure, and the modern theory of dilute solutions. A brief account of the theory of vegetable tanning has also been included in the chapter dealing with adsorption and membrane equilibria.

In addition to the books mentioned in the preface to the first edition, I have further to acknowledge my indebtedness to the following: Washburn's *Principles of Physical Chemistry*, Sackur's *Thermochemistry and Thermodynamics* (translated by Gibson), *X Rays and Crystal Structure* by W. H. and W. L. Bragg, Tutton's *Crystallography and Practical Crystal Measurement*, Nernst's *Solid State of Matter*, and Pollitzer's article on Nernst's Heat Theorem in *Ahren's Sammlung*.

I am indebted to Professor Bragg and to Messrs. G. Bell & Sons for permission to use certain diagrams from the book on Crystal Structure mentioned above. In the same connection I am indebted to the Council of the Chemical Society for permission to use two plates from the *Transactions*, vol. cix., 1916. Similar acknowledgment is due to Messrs. Macmillan for certain diagrams from Tutton's *Crystallography* referred to above. I have also to thank various correspondents who have kindly pointed out certain inaccuracies in the former edition.

Finally, I desire to express my thanks to Dr. W. B. Tuck for his kindness in reading the proofs of this edition, and also my sense of obligation to my colleague, Mr. James Rice, M.A., for much assistance generously given at all times, and in particular for Appendices I. and II. to Vol. III.

W. C. McC. LEWIS.

MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

PREFACE TO FIRST EDITION.

THIS book is intended to be used as a general textbook of physical chemistry by those who already possess some knowledge of both physics and chemistry. As there are at the present time several excellent treatises on elementary physical chemistry in English, it would obviously be fulfilling no good purpose to simply add another covering much the same ground. I have therefore aimed at making this book fairly comprehensive by including as far as was feasible some account of recent investigation, such for example as: the structure of the atom, the theory of concentrated solutions, capillary chemistry, Nernst's theorem of heat, the thermodynamics of photochemical reactions, and the application of the Planck-Einstein "Energie Quanta" to the specific heat of solids. Besides these recently examined problems, about which there is still considerable speculation, the fundamental principles and their applications which find a place in other books have likewise been incorporated here. At the same time I would suggest to the reader the advisability of first familiarising himself with the broad outlines of the subject, such as will be found, for example, in Walker's *Introduction to Physical Chemistry* or Senter's *Outlines of Physical Chemistry*.

The title which has been employed requires, perhaps, a word of explanation. The "System" consists in regarding all physicochemical phenomena as being capable of separation into two classes: first, phenomena exhibited by material systems when *in* a state of equilibrium; and, secondly, phenomena exhibited by material systems which have *not* reached a state of equilibrium. It is clear that this is not only a perfectly natural division, but likewise a perfectly general one, since any conceivable material system must belong to one class or the other. By emphasising this idea I hope to have impressed upon the reader's mind the fundamental co-relations which exist between what might at first sight appear very widely different phenomena. It has been my endeavour to get as far away as possible from the "selected chapter" method of treatment, which however necessary and suitable in a preliminary accumulation of facts, is very liable to cause the student to lose sight altogether of the essential unity of his subject.

The scientific treatment of any set of phenomena consists in applying the minimum of general principles or theories which can afford a reasonable explanation of the behaviour of matter under given conditions, and predict its behaviour under new conditions. The principles referred to as far as physics and chemistry are concerned are the kinetic theory and thermodynamics. In the kinetic method of treatment emphasis is laid upon the actual molecular mechanism of a given process; in the thermodynamic method the emphasis is laid upon the energy changes involved. Both methods should be familiar to anyone who undertakes the task of original investigation. Since a knowledge of the fundamental laws of the kinetic theory (including statistical mechanics) and thermodynamics is of such importance, some account—necessarily brief—has been given in this book. Of course, one might commence by writing an introductory chapter dealing with these various principles and then proceed to apply them indiscriminately to the phenomena dealt with. Anyone with teaching experience, however, will appreciate the fact that this method has the very serious drawback of bringing the reader at an early stage into contact with what is certainly the most difficult part of the subject, namely, the fundamental principles of thermodynamics and statistical mechanics. I have therefore divided the book into three parts, in which the phenomena exhibited by systems in equilibrium and not in equilibrium are treated, first, from the "classical" kinetic standpoint only; then independently from the thermodynamic; and finally from the standpoint of thermodynamics and the new or "modified" principles of statistical mechanics. I would only like to repeat that the "system" of classification upon which this book is based does *not* consist in the division into parts just mentioned, which latter is a purely arbitrary division and is only introduced for the purpose of making the book as readable as possible from the student's point of view. Further, it has been found desirable to divide the work into two volumes. Vol. I. contains Part I., and is briefly entitled "Kinetic Theory"; Vol. II. contains Parts II. and III., and is entitled "Thermodynamics and Statistical Mechanics".

As regards the thermodynamical treatment, it will be seen that the concept of "maximum work" and "free energy" has been employed practically to the exclusion of others. I have found by experience that this is more easily grasped than the idea of entropy, although I suppose that ultimately this must be something of a mental delusion.

Another feature to which I should like to draw attention is the intentional employment of the investigator's actual words where this is at all possible. It seems to me that in ascribing any scientific statement to an author it is only fair to reduce the editorial condensation process to a minimum. Of course, scientific papers as they appear in the journals are, as a rule, unsuitable for direct incorporation into a book of this nature and size, but I have attempted to reproduce them, at least in part, in the case of a few of the *classic* papers in physical chemistry with which one associates the names of van 't Hoff, Ostwald, Arrhenius, and Nernst. Nowadays one expects that the language difficulty will not be a serious one in the matter of reading foreign memoirs; though anyone who wishes to read these classic memoirs in their entirety in English will find a few of them scattered through the *Philosophical Magazine*, or more readily available in Harper's Scientific Memoir Series, edited by Ames.

As regards the subject-matter actually dealt with in this book, it will be observed that the relations of physical properties to chemical constitution and other purely stoicheiometrical relations have been omitted, since in my opinion a proper appreciation of what has been done here can only be obtained through the medium of a volume specially devoted to the subject, in which there is sufficient space for the comparison of a large collection of numerical data, such as one finds, for example, in S. Young's *Stoichiometry* and S. Smiles' *Relation of Chemical Constitution to some Physical Properties.*

As this is one of the series of textbooks edited by Sir William Ramsay, I have not hesitated to avail myself of those already published in the matter of many of the illustrative examples. I have also given numerous references where further information upon any subject is desirable not only to this series but still more to the original papers themselves.

In addition to references in the text itself, I should also like to acknowledge in this place my indebtedness to other works already published, namely: Ostwald's *Lehrbuch*, Nernst's *Theoretical Chemistry*, Nernst's *Applications of Thermodynamics to Chemistry*, van 't Hoff's *Lectures*, Haber's *Thermodynamics of*

Technical Gas Reactions, Walker's *Introduction to Physical Chemistry*, Lehfeldt's *Textbook of Physical Chemistry*, Abegg's *Electrolytic Dissociation Theory*, Arrhenius' *Electrochemistry*, Arrhenius' *Theories of Chemistry*, Le Blanc's *Electrochemistry*, Sackur's *Chemische Affinität* (Wissenschaft Series), Sackur's *Thermochemie und Thermodynamik*, Knox's *Physico-Chemical Calculations*, Kuenen's *Die Zustandsgleichung der Gase und Flüssigkeiten* (Wissenschaft Series), Bancroft's *Phase Rule*, Sir J. J. Thomson's *Electricity and Matter*, Sir J. J. Thomson's *Corpuscular Theory of Matter*, Preston's *Heat*, Freundlich's *Kapillarchemie*, Drude's *Optics*, Risteen's *Molecules and Molecular Magnitudes*, Perrin's *Brownian Movement and Molecular Reality*, Weigert's *Chemische Einwirkung des Lichtes* (*Ahren's Sammlung*), N. Campbell's *Modern Electrical Theory*. As regards symbols, I have employed to a considerable extent those recommended by the International Commission for the Unification of Physico-Chemical Symbols (1914). For this information I am indebted to the Secretary of the Committee, Professor Alexander Findlay.

I would also take this opportunity of expressing my warmest thanks for the assistance which I have received on various occasions from my colleagues and friends, Professor F. G. Donnan, F.R.S., University College, London; Professor A. W. Porter, F.R.S., University College, London; Professor N. T. M. Wilsmore, University of Western Australia, Perth; and Professor W. B. Morton, Queen's University, Belfast.

TABLE OF CONTENTS OF VOL. I.

Chart indicating the general system or scheme of subdivision . . *Frontispiece*

VOLUME I.

CONSIDERATIONS BASED UPON THE KINETIC THEORY.

CHAPTER I.

PAGE

Introductory—Molecules, atoms, and electrons—Elements of the kinetic theory—Molecular reality—Radioactivity—Transmutation of the elements .

CHAPTER II.

Distribution of molecules in space—Physical equilibrium—The continuity of the liquid and gaseous states from the kinetic standpoint—The solid (crystalline) state—Distribution of atoms in space (in crystals) . . 54

CHAPTER III.

Chemical equilibrium in homogeneous systems from the kinetic standpoint—Gaseous systems—Deduction of the law of mass action—Reactions in gaseous systems involving no change in the total number of molecules—Reactions involving a change in the number of molecules—Effect of change of temperature and pressure upon the equilibrium constant . . 116

CHAPTER IV.

Chemical equilibrium in homogeneous systems (*continued*)—Liquid mixtures—Solutions—Properties of solutions 155

CHAPTER V.

Chemical equilibrium in homogeneous systems (*continued*)—Mechanism of electrolytic conduction in solutions—The theory of electrolytic dissociation in aqueous solutions—Electrolytic dissociation in non-aqueous solutions . 188

CHAPTER VI.

Chemical equilibrium in homogeneous systems (*continued*)—Solid solutions . 282

CHAPTER VII.

PAGE

Chemical equilibrium in heterogeneous systems from the kinetic standpoint (effects due to capillarity, radiation, etc., being absent)—Nernst's Distribution Law—Gas-liquid systems—Liquid-liquid systems—Gas-solid systems — Solid-solid systems — Solid-liquid systems — Solubility and "solubility product" 288

CHAPTER VIII.

Chemical equilibrium in heterogeneous systems modified by capillary and electro-capillary effects—Colloidal solutions 326

CHAPTER IX.

Systems not in equilibrium—Treatment from the kinetic standpoint—*Homogeneous Systems:* Diffusion of solutes in a solution—Reaction velocity—Types of reactions —Catalysis 376

CHAPTER X.

Systems not in equilibrium—*Heterogeneous Systems:* Nernst's theory of reaction velocity—Catalysis—Langmuir's theory of surface action . . 444

SUBJECT INDEX 483

AUTHOR INDEX 490

(END OF VOLUME I.)

A SYSTEM OF
PHYSICAL CHEMISTRY

VOLUME I.

CONSIDERATIONS BASED UPON THE KINETIC THEORY.

CHAPTER I.

Introductory—Molecules, atoms, and electrons—Elements of the Kinetic Theory—Molecular reality—Radioactivity—Transmutation of the elements.

THE KINETIC MOLECULAR THEORY OF THE CONSTITUTION OF MATTER.

IT would be futile within the limits of an introductory chapter to attempt to give any concise account of the kinetic theory of matter. The student is assumed to be familiar with the general outlines of the subject, especially as regards the gaseous state. For the sake, however, of allowing us to gain some quantitative ideas of the processes which occur in molecular, and in general, in chemical processes, it will be advantageous to present at least some of the numerical *results* which have been obtained. For further information the reader is referred to Meyer's *Kinetic Theory of Gases*, translated by Baynes; Jeans' *Dynamical Theory of Gases*; and Byk's *Kinetische Theorie der Gase.*

SOME OF THE MORE IMPORTANT MAGNITUDES IN MOLECULAR PHYSICS, PRIOR TO THE WORK OF EINSTEIN, PERRIN, SVEDBERG, AND MILLIKAN.

According to the molecular theory, all matter is composed of small particles or molecules which are in rapid and irregular motion, the amplitude of such motion mainly determining whether the matter exists in the solid, liquid, or gaseous *state*. As is well known, the gaseous state, in which the molecules are on the average farther apart than in the other states, and likewise in more violent motion,[1] has lent itself most readily to theoretical treatment. For this reason we shall, to a large extent, limit ourselves to a brief consideration of the gaseous state. The first magnitude of interest is the *mean free path* of a molecule, that is the average distance traversed by a molecule between two successive collisions with other molecules. In a gas this is very large compared with the actual dimensions of the molecules themselves. In liquids and solids, on the other hand, the mean free path is of much the same order of magnitude as the molecular diameter itself. The next magnitude to be considered is the *velocity* of the molecules. The molecules in a gas do not all possess the same velocity. Even if this were momentarily the case, it can be shown on the theory of probability that the collisions would quickly destroy the equality. The enormous number of molecules even in a cubic millimetre of gas precludes any attempt to deal with the velocities of the individual molecules. The best we can do is to obtain a value for the *average velocity*. The problem of the distribution of velocities amongst the molecules of a gas has been solved in general terms by Clerk Maxwell in the theorem named after him.

---

[1] This must not be taken as meaning necessarily greater *energy* of translation.

STATEMENT OF MAXWELL'S THEOREM OF DISTRIBUTION OF VELOCITIES.

If we consider a system consisting of elastic spheres, *i.e.* molecules, in motion, the result of such motion will be to set up a certain state called a statistical equilibrium, such that the number (dn) of spheres having velocities lying between $\bar{v}$ and ($\bar{v} + d\bar{v}$) is given according to Maxwell by the relation—

$$dn = \frac{4n}{a^3\sqrt{\pi}} \, . \, e^{-\frac{\bar{v}^2}{a^2}} \, . \, \bar{v}^2 d\bar{v} \quad . \quad . \quad . \quad (1)$$

where n denotes the total number of spheres in the system, e is the base of natural logarithms, and a is a constant. We have to distinguish two closely related terms, namely, the mean or *average velocity* $\bar{v}_0$, which is simply the sum of all the velocities at a given moment divided by the number of molecules, and, secondly, the *root-mean-square-velocity* denoted by u. This quantity is such that its square is the sum of the squares of each separate velocity divided by the number of molecules.

That is $$u^2 = \frac{\bar{v}_1^2 + \bar{v}_2^2 + \bar{v}_3^2 + \text{etc.}}{n}.$$

It can be shown that u and $\bar{v}_0$ are connected by the relation—

$$\bar{v}_0 = \frac{4}{\sqrt{6\pi}} u = 0{\cdot}9213u.$$

That is, the average velocity is nearly, but not quite so great as the root-mean-square-velocity. The importance of the latter term is apparent when we remember that the kinetic energy of a molecule whose mass is m is given by the expression $\frac{1}{2}mu^2$.

We can best illustrate the Maxwell Theorem, which is simply equation (1), by means of a graph (Fig. 1) in which the ordinates denote number of molecules or rather fractions of the total n, and the abscissæ denote velocities. The ordinate for any value of $\bar{v}$ is proportional to the number of molecules having a velocity between $\bar{v}$ and $(\bar{v} + d\bar{v})$. It will be observed that the greater majority of the molecules present in the system are represented by an area the limits of which are not very different from $\bar{v}_0$, the average value. Since the curve approaches the horizontal axis on each side of the maximum, we can infer that there are a very few molecules practically motionless, and likewise a very few with extremely great velocity.

DEFINITION OF TEMPERATURE FROM THE KINETIC STANDPOINT.

According to the kinetic theory the temperature of a system corresponds to a certain value of the mean kinetic energy of translation of the molecules, namely $\frac{1}{2}mu^2$; so that if the temperature of a body be kept constant, the mean kinetic energy of the molecules is likewise constant. The reasonableness of this assumption is clearer if we consider the process of cooling a body. On this view, cooling a body is the same thing as decreasing the kinetic energy of the molecules, and one might imagine the cooling process continued until the translational motion of the molecules would finally cease. At this point the system has reached what is known as the "*absolute zero*" of temperature. With the help of the kinetic theory applied to the thermal expansion of gases we can calculate that the absolute zero is 273° below the freezing-point of water, or simply − 273° C. The behaviour of matter at this point is practically inconceivable to us, although one must not imagine that even at the absolute zero the body possesses no energy at all. It certainly possesses no kinetic energy in the form of translation. The question of the energy possessed by a substance at the absolute zero will be taken up in connection with Nernst's Heat Theorem (Vol. II., Chap. XIII.) as well as in connection with the "Quantum Theory" (Vol. III.).

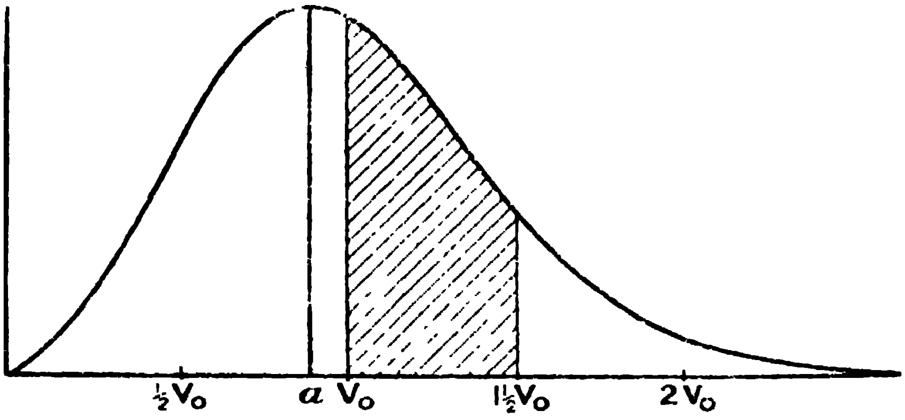


FIG. 1.

The Pressure Exerted by a Gas. Boyle's Law, Charles' or Gay-Lussac's Law, and the Hypothesis of Avogadro.

The following is not a rigid proof of Boyle's Law, but it is at least approximately correct.

Consider a large mass of gas at a given temperature, and suppose that a unit cube of the gas contains n molecules. The molecules are supposed all to possess the same velocity u. The mass of each molecule is m. The molecules move in all directions in the actual case, but for simplicity we shall consider that they may be divided into sets. For the moment we are regarding the walls of the cube as impermeable to the gas. Consider one molecule starting from one wall of the cube and moving in a straight line perpendicularly to the opposite wall where it rebounds, the change of momentum being $2mu$. Since the velocity is u, the molecule traverses u cms. per second, or passes over 1 cm., that is from wall to wall, u times in one second. That is, it strikes the wall u times per second,[1] and hence the total change in momentum per second is $2mu^2$. If there are n molecules present in the cube, we can imagine equal numbers to be travelling towards each of the six walls at the same instant. That is, at any instant $\frac{n}{6}$ molecules are travelling towards a certain wall, and when they strike they exert pressure on that wall. The total change in momentum per second due to the molecules striking one wall is $\frac{n}{6} \times 2mu^2$ or $\frac{1}{3}nmu^2$. Since the wall is of unit area the force exerted upon it is identical with the pressure p of the gas. Hence, we obtain the relation

$$p = \tfrac{1}{3}nmu^2.$$

Further, since nm represents the total mass of the gas in the unit cube, the quantity $\frac{nm}{1}$ c.c. is simply the density ρ of the gas, and therefore one may write—

$$p = \tfrac{1}{3}\rho u^2.$$

Also since the density ρ is the ratio of the total mass of gas M (which occupies the volume v) to the volume v, we can write

$$p = \tfrac{1}{3}\frac{M}{v}u^2, \text{ or } pv = \tfrac{1}{3}Mu^2.$$

---

[1] Actually the molecule which starts from the right-hand side strikes the left-hand wall once every *two* seconds and the right-hand wall just as often. This would make the number of collisions per second upon the left-hand wall due to this particular molecule only $\frac{u}{2}$. During the same second this molecule has, however, bombarded the right-hand wall $\frac{u}{2}$ times also, and every molecule may be regarded as thus striking two walls $\frac{u}{2}$ times *each* per second. Evidently the total bombardment is just equivalent to each molecule striking *one* wall only (say the left) u times per second.

But if the temperature of the gas be kept constant its total kinetic energy, which is $\frac{1}{2}Mu^2$, is likewise constant, and hence $\frac{1}{3}Mu^2$ is necessarily constant, so that one obtains—

$$pv = \text{constant},$$

which is Boyle's Law for gases. Further, Charles' or Gay-Lussac's Law for gases states that if the pressure of a given mass of gas be kept constant and the temperature be altered, the volume varies as the (absolute) temperature; or what amounts to the same, if the volume be kept constant the pressure varies as the (absolute) temperature. Boyle's and Charles' Laws may be combined into one expression, thus—

$$\frac{pv}{T} = \text{constant},$$

and this expression follows at once from that already deduced upon the basis of the kinetic theory, according to which $\frac{1}{2}mu^2$, and therefore $\frac{1}{3}mu^2$, is proportional to the absolute temperature T, so that we can write $pv = \text{constant} \times T$,

or
$$\frac{pv}{T} = \text{constant}.$$

Avogadro's Hypothesis may likewise be shown to be in agreement with the kinetic theory. According to this hypothesis, equal volumes of any gases at the same temperature and pressure contain the same number of molecules. Consider any two gases. The pressure p exerted by the first at a given temperature may be written

$$p = \frac{1}{3}n_1m_1u_1^2$$

where n_1 is the number of molecules in unit volume, m_1 is the mass of each molecule, and u_1^2 the mean square velocity of the molecules. Similarly, the same pressure p exerted by the second gas may be written—

$$p = \frac{1}{3}n_2m_2u_2^2.$$

Hence
$$n_1m_1u_1^2 = n_2m_2u_2^2.$$

Since the gases are likewise at the same temperature, the mean kinetic energies of the molecules of each gas are the same; that is

$$\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2.$$

Combining these two equations, one finds that

$$n_1 = n_2.$$

That is, the number of molecules in unit volume (*i.e.* the same volume for each gas) is the same for both, which is Avogadro's Hypothesis.

THE AVERAGE MOLECULAR VELOCITIES IN VARIOUS GASES AT 0° C.

It is found as a result of experiment that under *normal* conditions—that is under 1 atmosphere pressure and at 0° C.—the density of hydrogen gas is very nearly 0·00009 gram per cubic centimetre. The expression

$$p = \tfrac{1}{3}\rho u^2$$

may thus be employed for the calculation of u, *viz.*:

$$u = \sqrt{\frac{3p}{\rho}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

All numerical values must of course be expressed in the same units (the C.G.S. system). In the case of hydrogen gas under *normal* conditions, $p = 1$ atmosphere $= 1·016 \times 10^6$ dynes per square centimetre, $\rho = 9 \times 10^{-5}$ grams per cubic centimetre, and hence

$$u = 1·8 \times 10^5 \text{ cms. per second.}$$

The average value $\bar{v}_0$ of the velocity is $0·9213u$, so that $\bar{v}_0$ for hydrogen at 0° C. and 760 mm. is $1·65 \times 10^5$ cms. per second. Other gases, such as oxygen, nitrogen, and carbon dioxide, have molecular velocities one-fourth to one-tenth of that possessed by the hydrogen molecule.

VISCOSITY OF GASES AND THE CALCULATION OF THE MEAN FREE PATH OF THE MOLECULES.

If a layer in a gas is caused to stream in any given direction, one may anticipate that owing to the frequent collisions between the molecules of the streaming layer and the contiguous molecules of the surrounding gas that the streaming motion would be partially transferred to the "stationary" gas layers, and as a whole the gas would begin to stream, except that layer which lies closest to the walls of the vessel. A certain amount of momentum has been transferred through the various layers of the gas, and hence in virtue of the streaming motion the molecules have exerted a force upon one another. This force is called viscosity. Viscosity is possessed even by a perfect gas, *i.e.* one which obeys Boyle's Law absolutely. This force is therefore not to be confounded with the forces of molecular attractions which, as we shall see later, are present in all actual gases and cause them to depart to greater or less extents from the ideal or perfect gas. Viscosity is sometimes called *internal friction*, and the coefficient of viscosity of any fluid—liquid or gas—is defined as the force per unit area exerted between two parallel layers, 1 cm. apart, when the velocity of streaming differs by unity in the two layers.

With the help of the kinetic theory it is possible to deduce a relation between the coefficient of viscosity η of a gas, and the mean free path λ, according to which—

$$\eta = \tfrac{1}{3}\rho\lambda u \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(see Meyer's *Kinetic Theory of Gases*, pp. 175 *seq.*), where ρ is density and u velocity.[1]

---

[1] It should be borne in mind that the u term for any gas is always very much greater than any streaming velocity which can be artificially set up.

Now we have already seen that the pressure p of the gas is given by

$$p = \tfrac{1}{3}\rho u^2$$

so that the above expression may be rewritten—

$$\lambda = \eta\sqrt{\frac{3}{p\rho}} \tag{4}$$

Since $p \propto \frac{1}{\rho}$ it follows that the viscosity of a gas is independent of the pressure which, though by no means an obvious result, has been completely verified by experiment.

For the present purpose, however, the importance of viscosity determinations lies in the fact that they permit of a calculation of the mean free path of the molecules—for example, by means of equation (4).

In the following table are given the coefficients of viscosity, the mean free paths, and the collision frequencies of a few gases (see Meyer's *Kinetic Theory*, p. 192) at normal temperature and pressure. The collision frequency is the root-mean-square-velocity u, divided by the mean free path λ.

Gas.	η.	λ cms.	Collision Frequency, or Number of Collisions per Second, $\times 10^{-6}$.
Hydrogen	$0{\cdot}0_4 86$	$0{\cdot}0_4 182$	9280
Nitrogen	$0{\cdot}0_3 166$	$0{\cdot}0_4 094$	4820
Oxygen	$0{\cdot}0_3 187$	$0{\cdot}0_4 100$	4280
Carbon dioxide . . .	$0{\cdot}0_3 138$	$0{\cdot}0_4 063$	5780
Carbon monoxide . . .	$0{\cdot}0_3 162$	$0{\cdot}0_4 092$	4920

Reference will be made later to Rankine's determinations of the relative viscosities of the rare gases.

MOLECULAR ATTRACTION IN GASES AND THE EFFECTIVE RANGE OF ATTRACTION.

Hitherto we have considered gases simply as systems of small spherical perfectly elastic particles in rapid motion, colliding frequently, but otherwise without influence upon one another. The study of actual gases has, however, shown that these assumptions are only approximately, not absolutely fulfilled (see Chap. II.). Boyle's Law, for example, at high pressures does not hold accurately even for gases such as hydrogen, oxygen, nitrogen, etc., which at ordinary temperatures are far above their liquefying points. As will be seen later, these and other discrepancies are attributable to two causes, one of which is the existence of attractive forces between the molecules of the gas, and the other is the magnitude and actual compressibility of the molecules themselves, which under high pressure can no longer be regarded as occupying a space which is negligible compared with the free space between them. The attractive forces referred to are only effective throughout an extremely small range, approximately 10^{-7} to 10^{-8} cm. Inside this range, however, the attractions may become enormously great. This effective range is known as "the range of molecular attraction". Of course, these forces are exerted theoretically to an infinite distance throughout space, but it is only within the extremely narrow limits mentioned that the attraction due to a molecule assumes any magnitude of importance. In the case of liquids, where the average distance apart of the molecules is less than the range of attraction, these forces may amount to several hundreds or even thousands of atmospheres reckoned across any unit area in the interior. To this is to be attributed the decreased freedom of motion possessed by the molecules of a liquid as compared with the molecules of a gas, and consequently the complete inapplicability of the simple gas laws.

The most direct means of showing that ordinary gases are not *perfect* or *ideal*—though nearly so—is afforded by the well-known porous plug experiment of Joule and Thomson (Lord Kelvin). In this experiment a gas is passed under high pressure through a porous plug, at the other side of which the pressure is kept low. Under these conditions it was shown by Joule and Thomson that the temperature of the gas differed on the two sides of the plug. For all ordinary gases except hydrogen the temperature on the low-pressure side was lower than that on the high-pressure side. In the case of hydrogen, the temperature effect was the reverse, but this was later shown to be due to the actual mean temperature of the experiment being too high for that gas. If the experiment be carried out at a very low mean temperature, hydrogen is found to behave like other gases. If these gases had been ideal gases, no change in temperature on passing through the plug would be expected.

Numerous attempts have been made from time to time to find out the law of molecular attraction, that is, how the force varies with the distance. It is certain that the law is not that which governs gravitational attraction, in which the force varies inversely as the square of the distance. Reference will only be made in the present instance to the law of attraction, which is involved in van der Waals' equation for fluids (Chap. II.). If we consider a unit area in the interior of a fluid, the force of attraction across the area depends upon the number of molecules spread over the unit surface, and likewise upon the distance apart of the molecules. If r is the average distance apart of the molecules, then the number of molecules per unit area is inversely proportional to r^2, and as the attractive force between any two molecules on opposite sides of the area varies inversely as some unknown function of the distance apart, which we may write in the form r^n, it follows that the attractive force exerted per unit area perpendicularly across the imaginary plane is proportional to $\frac{1}{r^{n+2}}$. Since the volume v of the fluid is proportional to r^3, the attractive force may be written as proportional to

$\overline{v^{\frac{n+2}{3}}}$. But according to van der Waals' equation, this force can be expressed by the term $\frac{a}{v^2}$, where a is a constant. To make these two expressions concordant, it is necessary that we put $n = 4$. That is, the van der Waals equation assumes that *the attraction between molecules varies inversely as the fourth power of the distance of the molecules apart.* It may be mentioned that under certain conditions electrical (and magnetic) attractions vary as this power (not simply as the inverse square). If we assume with Sutherland (*Phil. Mag.* [6], **4**, 625, 1902) and Reinganum (*Physikal. Zeitschr.*, **2**, 241, 1901 ; Drude's *Annalen*, **10**, 334, 1903) that equal positive and negative charges are present in molecules, and these charges are concentrated wholly or partly in points, then the molecule will represent what is known as an "electrical doublet," and the inverse fourth-power law will hold good for such a system, just as it does in the case of two small magnets.

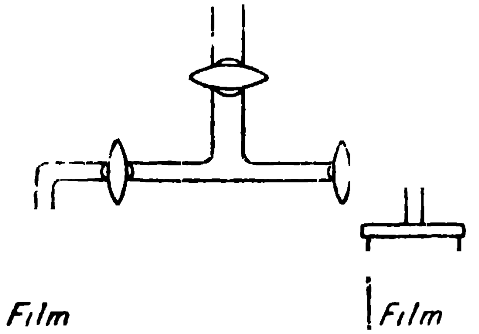


FIG. 2.

From this point of view it would seem, therefore, that molecular attraction may be ultimately electrical in origin. It must be pointed out, however, that it is by no means certain that the inverse fourth-power law is the correct one. Inverse fifth- and even sixth-power laws have been found to be fairly applicable, so that there is doubt as to whether these molecular attractions can be expressed in this simple "power" form at all. For a further discussion of the question of molecular attraction reference is made to Sutherland's earlier papers (*Phil. Mag.*, **22**, 81, 1886 ; **27**, 305, 1889 ; **35**, 211 ; **36**, 150, 507, 1893), as well as to the chapter upon the subject in J. P. Kuenen's *Die Zustandsgleichung der Gase und Flüssigkeiten* (Wissenschaft Series).

We now pass on to the question of the determination of the *range* of molecular attraction.

The most frequently employed value, namely, 5×10^{-6} cm., is that which is obtained by Quincke's "Wedge" method. This value is approximately 100 to 200 times greater than the actual diameters of the molecules of ordinary fluids. By comparison with other results, however, it appears likely that Quincke's estimate is certainly too large. A better method consists in measuring the limiting thickness of a stable soap film which was carried out by Reinold and Rücker (*Phil. Trans.*, **177**, Part II., 627, 1886). Two cylindrical soap films were obtained by means of the apparatus shown diagrammatically in Fig. 2.[1] One film could be maintained at constant thickness (by passing an electrical current through it vertically upward) and therefore at constant surface tension, while the other was allowed to drain, producing changes in the thickness, which should be indicated by changes in the surface tension when the film has thinned down to the region of the molecular range of attraction. Any change in the surface tension would be immediately indicated by a bulging of one of the cylinders and a contraction of the other. It was found that the tension was constant down to the stage of tenuity when the film was showing the black of the first order of Newton's scale of colour. By measurements of optical interference as well as by electrical measurements, Reinold and Rücker were able to calculate the thickness of the black film and found it to be $12\mu\mu$ or 12×10^{-7} cm. This might at first sight appear to be a fairly accurate value for the range of attraction, but this is rendered much less conclusive owing to the existence of certain phenomena observed by Reinold and Rücker themselves. Thus it was shown that the black and coloured parts of the film were *sharply* separated, so that the film is really discontinuous, in some places the thickness is 250 times that in others (*i.e.* the black portions), and yet apparently the film as a whole is in equilibrium. This suggests that between $12\mu\mu$ and $100\mu\mu$ the film is unstable, but is stable at either limit. On allowing the film to drain still further, so that the thinnest parts were less than $12\mu\mu$, these parts became unstable. Later, Johonnot (*Phil. Mag.*, **47**, 501, 1899) showed in the case of sodium oleate films that the black part itself consists of two portions, one $12\mu\mu$ thick, the other $6\mu\mu$. The general result of these very complex phenomena appears to be that the attraction exerted by a molecule ceases to be effective at a distance of $5 - 10 \times 10^{-7}$ cm.

Mention should also be made of a calculation carried out by Lippman, based upon electro-capillary observations (*Comptes Rendus*, **95**, 686, 1882). Lippman obtained the value 3×10^{-8} cm. for the thickness of the "electrical double layer" (see Chap. VIII. on Capillary Effects) at the interface, where the mercury and sulphuric acid solution met; and we may possibly identify this with the range of molecular attraction. Assuming this to be the case, and introducing one or two obvious corrections into Lippman's calculation, one obtains the value $2{\cdot}4 \times 10^{-7}$ cm. More recent work of the writer (Lewis, *Phil. Mag.*, Jan., 1913, p. 61) leads to the conclusion that the range is of the order 10^{-8} cm.

---

[1] For a more detailed account, see Poynting and Thomson, *Properties of Matter.*

ATTEMPTS TO DETERMINE THE ACTUAL DIMENSIONS OF MOLECULES.
(See Jeans, *Dynamical Theory of Gases.*)

(1) An early attempt to determine the aggregate volume occupied by the molecules of a gas consisted in applying the expression—

$$K = \frac{1 + 2\epsilon}{1 - \epsilon}$$

where K is the dielectric constant of the gas, and ϵ is the ratio which the actual volume of the molecules bears to the observed volume. The expression is based on the Clausius-Mosotti theory of dielectrics, and the molecules are assumed to be conductors. Mercury vapour would probably correspond to these conditions, but its dielectric constant is not known. Although it is straining the applicability of the expression, it has been employed in connection with a number of gases, including the rare gases of the atmosphere. According to the Maxwell theory of light, we can write—

$$K = \mu^2$$

where μ is the refractive index of the gas for very long waves. Substituting this in the above expression, one obtains—

$$\epsilon = \frac{\mu^2 - 1}{\mu^2 + 2}.$$

A further approximation is made by employing determinations of μ made for wave-lengths of the visible region (which are relatively short waves). The results, however, are of considerable interest. Cuthbertson (*Phil. Mag.*, **21**, 69, 1911) has recently determined ϵ for the rare gases, the values being as follows :—

He	Ne	Ar	Kr	Xe
$0{\cdot}0_4231$	$0{\cdot}0_4444$	$0{\cdot}0_31848$	$0{\cdot}0_32791$	$0{\cdot}0_34545$

These numbers show what a very small fraction of the total volume is actually occupied by the molecules themselves. If one knows the actual number of molecules in a given volume, it is easy to calculate the volume of each, and hence the diameter.

The most accurate method of determining the actual number of molecules in a given volume of a gas is the Perrin method, which will be described in some detail later.

(2) Another method of calculating the radius σ of a molecule is based upon the kinetic theory (*cf.* Meyer, *Kinetic Theory*, p. 300), and involves a knowledge of the mean free path λ, which can be obtained from viscosity determinations. The most accurate viscosity measurements are those of A. O. Rankine (*Proc. Roy. Soc.*, A. **83**, 516, 1910; **84**, 181, 1910; **86**, 162, 1912; **91**, 201, 1915; *Phil. Mag.*, **29**, 552, 1915), who has employed his data to calculate the molecular radius.

According to Maxwell the following relation holds :—

$$\eta = 0{\cdot}307\rho\lambda\sqrt{\frac{3p}{\rho}}$$

where η is the viscosity of the gas, ρ its density, p the pressure, λ the mean free path. This enables us to calculate λ. Further, λ is connected with the radius σ of the molecule by the relation :—

$$\lambda = \frac{1}{\sqrt{2}\,.\,n\pi\sigma^2}$$

where n is the number of molecules in unit volume of the gas. These relations are based on the assumption that there are no forces of attraction between the molecules. Since forces of attraction do exist, the value of σ obtained by these equations is not accurate. Sutherland has shown (*Phil. Mag.*, **36**, 507, 1893) that the true radius σ_0 can be calculated from σ by means of the relation—

$$\sigma_0 = \qquad + \frac{C}{T}\Big)^{\frac{1}{2}}$$

where C is a constant, which can be calculated from a determination of the variation of viscosity with temperature.

The following values of the molecular radii have been obtained by Rankine :—

Gas.	Relative Radius.	Absolute Radius.	ϵ.
Helium . . .	1·00	$0·84 \times 10^{-8}$ cm.	$0·43 \times 10^{-4}$
Neon . . .	1·21	1·02	0·77
Argon . . .	1·53	1·28	1·54
Krypton . . .	1·65	1·38	1·94
Xenon . . .	1·83	1·53	2·65

The absolute value of the radius is obtained from the relative value by multiplying by the factor $0·84 \times 10^{-8}$. The quantity ϵ, which is the actual volume of the molecules in 1 c.c. of the gas, is given by the expression $4\pi n\sigma_0^3/3$. The value of n, at normal temperature and pressure, is $2·7 \times 10^{19}$ (*vide infra*), from which the values of ϵ, given in the last column, have been calculated. These values of ϵ are of the same order of magnitude as those obtained by the refractive index method.

The following values of the molecular radii have been obtained by Rankine for the halogen gases :—

Chlorine	1·60 × 10·
Bromine	1·71
Iodine .	1·88

It is assumed in all these calculations that the molecules are spherical, an assumption which is only approximately true.

(3) Another method of determining the size of molecules depends on the application of the so-called "equation of state" of van der Waals. This equation is simply a modified form of the gas equation, $pv = RT$, when account is taken of the "lack of perfection" of actual

gases owing to the presence of molecular attraction and the actual space taken up by the molecules themselves. The equation is considered at some length in Chap. II. For the present we shall simply assume its validity. The equation is usually written in the form—

$$\left(p + \frac{a}{v_2}\right)(v - b) = \mathrm{RT}.$$

The term $\frac{a}{v^2}$ represents the correction term due to the molecular attractions, a being taken to be a constant and v the volume (of the gas or of the liquid). The term b is the limiting value which the volume v would assume under practically infinitely high pressure. It can be easily shown that if the molecules are spheres, and if, under the pressure referred to, the molecules actually touch one another, then the volume term b will be $\frac{7}{8}$ of their actual volume.[1] If we are considering unit volume of the gas, that is $v = 1$, then $\frac{8}{7}b$ is simply ϵ. With the help of experimentally determined values of b it is therefore possible to determine the diameter of the molecules. The results obtained show that the order of magnitude is 10^{-8} cm.

(4) In 1858 Clausius put forward the following theorem: the ratio of the total space occupied by a gas to the actual volume of the molecules contained in the same space is equal to $\frac{8\lambda}{2\sigma}$, where λ and σ have their usual significance. This was deduced prior to Maxwell's theorem of distribution of velocities among the molecules. On introducing the necessary correction, one obtains—

$$\frac{1}{\epsilon} = \frac{8{\cdot}5\lambda}{2\sigma}.$$

Employing the values of ϵ and λ previously obtained, one can calculate σ. The following table contains a few of the results:—

Gas.	ϵ.	2σ.
Hydrogen	$0{\cdot}0_3 33$	$4{\cdot}7 \times 10^{-8}$ cm.
Nitrogen	$0{\cdot}0_3 87$	$6{\cdot}7 \times 10^{-8}$,,
Oxygen	$0{\cdot}0_3 74$	$6{\cdot}1 \times 10^{-8}$,,
Carbon dioxide . . .	$0{\cdot}0_3 72$	$3{\cdot}0 \times 10^{-8}$,,

The values of σ obtained by this method are of the same order of magnitude as those given by other methods.

Values for σ have likewise been obtained from measurements of heat conduction and diffusion in gases. These are fully discussed in Jeans'

---

[1] Van der Waals has, however, shown that the b of his equation is four times the actual volume of the molecules. The apparent discrepancy comes in because if all the molecules were to touch one another simultaneously no kinetic movement would be possible, a state of affairs only realisable at absolute zero. This distinction, however, does not affect the order of magnitude of the quantity dealt with here

Dynamical Theory of Gases. The results agree well with those obtained from viscosity measurements.

(5) Lord Rayleigh's surface tension method. Every liquid is characterised by the existence of a tension over its surface which acts as if the surface layer were an elastic film. This "surface tension" is very sensitive to the presence of impurities in the liquid. It was noticed long ago that if pieces of camphor be placed upon a water surface they move about rapidly, the motion being due to local alterations in the surface tension of the water surrounding the pieces of camphor. It was also observed that the camphor movements could be stopped by the addition of a very small trace of oil to the water surface. Lord Rayleigh estimated the minimal quantity of oil which had to be added to a known area of water to cause the movements just to cease. He thus found the "critical" thickness of the oil layer required. This was approximately $1 \cdot 6 \times 10^{-7}$ cm. Now, it cannot be assumed that the oil layer was just 1 molecule thick,[1] but it cannot have been less than this, so that the above value represents a *major limit* of the molecular diameter. It is five to ten times that previously obtained.

(6) Among other methods which yield a major limit may be mentioned that of Oberbeck (*Wied. Ann.*, **31**, 337, 1887), who found that a coating of metal 3×10^{-7} cm. in thickness was sufficient to alter the electrical potential of a platinum electrode (probably by the formation of an alloy on the surface). Further, Wiener found that a film of silver 2×10^{-8} cm. in thickness was sufficient to alter appreciably the phase of reflected light.

(7) The last method to be mentioned deals with the size of atoms (or molecules) of metals, and is due to Lord Kelvin (*Popular Lectures and Addresses*, Vol. I., p. 168). The principle of the method consists in measuring the amount of electrical work done in bringing two charged metal plates close to one another. If one brings two pieces of zinc and copper into contact at one corner they become electrified, and attract one another. Lord Kelvin calculated that when the air space between them is 10^{-5} cm. the attraction per unit area is 2 grams weight. One can imagine a pile of such plates built up with zinc and copper alternately, the air spaces being 10^{-5} cm., until the height of the pile is 1 cm. The electrical work done in the process of building up is 2 cm. grams. The whole mass of metal is 8 grams, and knowing the mean specific heat, it can be easily calculated that if this electrical work be converted into heat, the consequent rise in temperature would be $\frac{1}{16120}$° C. "Now let the thickness of each piece of metal and of each intervening space be 10^{-8} cm. The work would be increased one-million fold unless 10^{-8} cm. approaches the smallness of a molecule. The heat equivalent would therefore be enough to raise the temperature of the material 62° C." As this is barely possible from what we know of the heat of combination of zinc and copper in forming an alloy, it is

---

[1] The recent investigations of Langmuir referred to in Chap. X. of this volume indicate that the oil layer *is* just 1 molecule thick.

reasonable to conclude that plates thinner than 10^{-8} cm. would be smaller than the atoms of the metals. It follows therefore that 10^{-8} cm. is the minimum admissible size of the atoms of copper and zinc, or what is the same thing, when these metals alloy, their atoms do not approach one another more closely than this. The method is, of course, very crude, but it is remarkable that we obtain once more a value of the same order of magnitude as that obtained in the case of gaseous substances.

The Most Probable Values for the Molecular Diameters of some Gases. (Sutherland, *Phil. Mag.*, **19**, 25, 1910.)

Sutherland assumes that there are $2·77 \times 10^{19}$ molecules of gas in 1 c.c. at normal temperature and pressure. This agrees well with Millikan's value (*Phil. Mag.*, **19**, 228, 1910), which will be considered later, namely, $2·76 \times 10^{19}$. Knowing the number of molecules per cubic centimetre, Sutherland recalculated the molecular diameters using the viscosity data given by Jeans. The following table contains the results:—

Gas.	Molecular Diameter in cms. × 10^8.	Gas.	Molecular Diameter in cms. × 10^8.
Hydrogen	2·17	Oxygen	2·71
Helium	1·97	Argon	2·66
Carbon monoxide	2·74	Carbon dioxide	2·90
Ethylene	3·31	Nitrous oxide (N_2O)	3·33
Nitrogen	2·95	Chlorine	3·74
Air	2·86		
Nitric oxide (NO)	2·59		

Evidence for the Real Existence of Molecules.

Hitherto we have found that the concept of molecules is a satisfactory working hypothesis by means of which the behaviour of gases (and to a less degree the behaviour of liquids) can be accounted for. No *direct* evidence, however, for the actual existence of very small discrete particles in rapid and continuous motion in a gas or liquid has yet been given. It is evident that if such can be given it places the kinetic theory upon a firmer basis. This is of special importance from the kinetic standpoint of physico-chemical processes. We shall therefore consider what evidence is available.

The Radiometer.—This instrument consists of a glass bulb, inside of which is pivoted a small paddle wheel with mica vanes, the vanes being blackened on one side. When the bulb is exhausted to a certain point, then on bringing a source of radiant heat near the vessel the paddle revolves, the unblackened sides of the vanes being foremost, *i.e.* in the direction of motion. This is explained as due to unequal bombardment of the sides of each vane by the molecules of the gas. The blackened side absorbs the radiant heat better than the unblackened, and hence the gas molecules in contact with the blackened side have imparted to them greater kinetic energy than those on the unblackened side. The molecules with greater kinetic energy strike the vane more vigorously than those on the unblackened side, and hence the vane is subjected to a net pressure which causes it to move with the unblackened side foremost. This is fairly direct evidence for the actual existence of molecules. It must be pointed out, however, that the phenomenon is not so simple as the above account of it might lead one to imagine. If the bulb is not exhausted at all, the vanes remain stationary. If the exhaustion is only moderate, the direction of motion is actually the reverse of that described. This is explained by saying that at moderate pressures the mean free path of the molecules is so small and the number of collisions so great that the accelerated molecules which fly off from the blackened surface beat back the molecules with which they come in contact, and hence cause a local *rarefaction* of the gas on the blackened side, with the result that the vane moves with the blackened side foremost. As far as they go radiometer effects are fairly direct evidence for the existence of molecules. The first really conclusive evidence, however, has come from a quite unexpected source, namely, the phenomenon known as "Brownian Movement," exhibited by small particles suspended in liquids.

BROWNIAN MOVEMENT AND MOLECULAR REALITY.[1]

If one examines with a microscope a liquid in which fine particles are suspended, such as an emulsion of mastic, or gamboge in water, or the still finer particles which are present in colloidal solutions of metals, hydroxides or sulphides (Chap. VIII.), which can be rendered visible by means of the ultra-microscope, we find in all cases that the particles are in a state of rapid and irregular motion. This was first noticed in 1827 by the botanist Brown. The cause of these movements has naturally been the subject of much investigation, but it was not until 1879 that Ramsay (*Proc. Glasgow Phil. Soc.*) for the first time showed that they are very probably due to the bombardment of the particles by the molecules of the liquid medium. In 1888 the French physical chemist Gouy independently arrived at the same conclusion. Gouy observed that the motion was not due to the light which necessarily passed through the liquid under examination, for he was able to reduce the intensity of the light to one-thousandth of its value without in the least affecting the movements. Neither is it due to convection currents in the liquid, for it persists after sufficient time has elapsed for thermal equilibrium to be established. Neither is it due to external vibration. Even the *nature* of the particles has very little influence upon the phenomenon, although their *size* is important, the smaller the particle the more vigorous the movement. The most remarkable feature is that the movement goes on ***indefinitely.*** No more satisfactory explanation has been put forward than that of Gouy, namely, that the movement is a direct consequence of the continuous irregular movements of the molecules of the medium. It serves therefore to visualise the movements of the molecules themselves. All this, however, is of a qualitative nature. We owe to Perrin the quantitative investigation of the phenomenon.

---

[1] See *Brownian Movement and Molecular Reality*, by J. Perrin, translated by F. Soddy (1910).

Assuming that the movement is due to molecular bombardment, Perrin sought to obtain, from measurements made upon the emulsion particles of mastic, rubber, and gamboge, values for what he calls the Avogadro Constant, namely, the actual number N of molecules in one grammole of a gas. N is known, at least roughly, from considerations with which we have already dealt in determining the size of the molecules. In the case of oxygen gas, for example, from the known value of ϵ one can calculate that N lies between 45×10^{22} and 200×10^{22}, the lower limit being probably the more correct. Also on the basis of the electromagnetic theory of radiation applied to the case of long (heat) waves, Lorentz has calculated[1] from Lummer and Pringsheim's data that $N = 77 \times 10^{22}$ (see Perrin, *l.c.*, pp. 88, 89).

Perrin's own method of investigation by means of the Brownian Movement may now be briefly outlined.

It has been shown that in the case of a gas the pressure p is represented by the expression—

$$p = \frac{1}{3}, \frac{nm}{v} u^2$$

where n is the number of molecules in v c.c., and m the mass of a single molecule. Rewriting the above in the form—

$$pv = \tfrac{1}{3} nmu^2$$

and denoting by w the mean kinetic energy of each molecule ($w = \frac{1}{2}mu^2$), we obtain the alternative form—

$$pv = \tfrac{2}{3} nw.$$

For a perfect gas the gas equation (with which the reader is assumed to be conversant) is $pv = \mathrm{RT}$, in which R has the value 1·985 calories per degree or $83{\cdot}2 \times 10^6$ c.g.s. units if the *mass* of gas considered be one grammole. Also, if we are considering one grammole, the number n can be written N, *i.e.* the number of molecules in one grammole of any gas. On combining the above two equations one obtains—

$$\tfrac{2}{3}\mathrm{N}w = \mathrm{RT}$$

or

$$w = \frac{3\mathrm{RT}}{2\mathrm{N}}.$$

Hence, if we can measure w, the mean kinetic energy of a molecule, we can calculate N, for the other terms are known. Since the above relation applies to the gaseous state, one might be inclined to think that to obtain a value for *w* we would have to confine ourselves to the gaseous state. This, however, is not necessary provided we assume the validity of the important generalisation known as the Law of Equipartition of Energy among the various particles constituting a system. By applying this principle it is possible to calculate *w* from the Brownian Movement of particles suspended in *liquids* and hence obtain a value for N. What is meant by the equipartition of energy as applied to this case may be most briefly given in Perrin's own words (Perrin, *l.c.*, pp. 18, 19):—

---

[1] An accurate determination of N can be obtained with the help of Planck's radiation equation (see Vol. III.).

"We have seen that the mean molecular energy is, at the same temperature, the same for all gases. This result remains valid when the gases are mixed. . . . For example, the molecules of carbon dioxide and water vapour, present in the air, must have the same mean kinetic energy in spite of the difference in their natures and masses. This invariability of molecular [kinetic] energy is not confined to the gaseous state, and the beautiful work of van 't Hoff[1] has established that it extends to the molecules of all dilute solutions. Let us imagine that a dilute solution is contained in a semi-permeable enclosure which separates it (the solution) from the pure solvent. We suppose this enclosure allows free passage to the molecules of the *solvent*, in consequence of which these molecules cannot develop any pressure, but that it stops the *dissolved* molecules. The impacts of these molecules against the enclosure will then develop an *osmotic* pressure P, and it is seen, if the reasoning is considered in detail, that the pressure produced by these impacts can be calculated as in the case of a gas, so that in consequence we write $Pv = \frac{2}{3}nW$, W signifying the mean kinetic energy of translation of each of the n molecules [of dissolved substance or 'solute'] contained in the volume v of the enclosure. Now van 't Hoff has observed that the experiments of Pfeffer give for the osmotic pressure the same value as that which would be exerted by the same mass of dissolved substance if it alone occupied in the *gaseous* state the volume of the enclosure. W is thus equal to w; the molecules of a dissolved substance have the same mean kinetic energy as in the gaseous state [at the same temperature]. . . . van 't Hoff's law tells us that a molecule of ethyl alcohol in solution in water has the same [kinetic] energy as one of the molecules of vapour over the solution. It would still have the same energy if it (the ethyl alcohol molecule) were present in chloroform (that is to say if it were surrounded by chloroform molecules) or even if it were in methyl or propyl alcohols. This indifference to the nature of the molecules of the liquid in which it moves makes it almost impossible to believe that it would not still have the same energy if it (the ethyl alcohol molecule) were in ethyl alcohol; that is, if it forms one of the molecules of pure ethyl alcohol. It therefore follows that the [kinetic] molecular energy is the same in a liquid as in a gas [at the same temperature], and we can now say:—

---

[1] Chapter IV.

"*At the same temperature all the molecules of all fluids have the same mean kinetic energy which is proportional to the absolute temperature.*

"But this proposition, already so general, can be still further enlarged. According to what we have just seen, the heavy molecules of sugar,[1] which move in an aqueous sugar solution, have the same mean kinetic energy as the lighter molecules of water. These sugar molecules contain 45 atoms; the molecules of sulphate of quinine contain more than 100 atoms, and the most complicated and heaviest molecules to which the laws of van 't Hoff can be extended may be cited. The applicability of the generalisation [of the equipartition of kinetic energy] does not appear to be limited to any *size* of molecule. Let us now consider a particle a little larger still, itself formed of several molecules, in a word, a speck of dust. Will it proceed to react towards the impacts of the molecules encompassing it according to a new law? Will it not comport itself simply as a very large molecule, in the sense that its mean kinetic energy has still the same value as that of an isolated molecule? This cannot be averred without hesitation, but the hypothesis at least is sufficiently plausible to make it worth while to discuss its consequences Here we are then taken back again to the observation of the particles of an emulsion, and to the study of this wonderful movement which most directly suggests the molecular hypothesis. But at the same time we are led to render the theory precise by saying, not only that each particle owes its movement to the impacts of the molecules of the liquid, but further that the energy maintained by the impacts is on the average equal to that of any one of these molecules. . . . So that if we find a means of calculating this granular energy [*i.e.* the kinetic energy of the particles or granules] in terms of measurable magnitudes we shall have at the same time a means of proving our theory."

PERRIN'S FIRST METHOD.

This method consisted in determining the distribution of the emulsion particles under the action of gravity. Just as air is densest at the surface of the earth, so an emulsion distributes itself in such a way that the lower layers have a higher concentration of granules than the upper layers. Let us imagine an emulsion filling a vertical cylinder of cross-sectional area s square cm. Consider a horizontal slice of the emulsion at a height h from the base. Suppose that at this level the number of granules is *n per unit volume.* Similarly, at a height $h + dh$ the number of granules per unit volume is $n - dn$ (as h increases the concentration of the granules decreases, hence the negative sign). The osmotic pressure of the granules at the height h is $\frac{2}{3}n\mathrm{W}$, where W is the mean kinetic energy of each granule. At the height $h + dh$ the osmotic pressure is $\frac{2}{3}(n - dn)\mathrm{W}$. The difference of osmotic pressure which exists between the two planes is $-\frac{2}{3}dn\mathrm{W}$. Now pressure denotes force per unit area, and hence the difference of the osmotic forces acting over the area s is $-\frac{2}{3}sdnW$. But the granules as a whole are in equilibrium, and therefore this difference of osmotic forces between the two planes must be balanced by the difference of the gravitational attractions exerted at the two planes. If ϕ is the volume of a single granule, D its density, δ the density of the liquid medium, and g the acceleration of gravity, then the effective weight or downward force exerted upon a single granule is $\phi(D - \delta)g$. The volume of liquid between the two planes considered is sdh, and if there are n granules per unit volume $\left(\text{more strictly } \frac{2n + dn}{2}\right)$, the total gravitational pull upon all the granules present between the two planes is—

---

[1] Pfeffer's experiments were carried out with solutions of cane sugar, and van 't Hoff showed that the osmotic pressure of dissolved sugar molecules obeyed the gas law, $pv = \mathrm{RT}$.

$$nsdh\phi(D - \delta)g.$$

It is this force which prevents the granules distributing themselves at the same concentration throughout the entire liquid between the two planes, and therefore it is this force which opposes and balances the osmotic force $-\frac{2}{3}sdnW$. Equating these two forces, we obtain—

$$-\tfrac{2}{3}sWdn = nsdh\phi(D - \delta)g.$$

We can integrate this expression so that it gives a relation between n_0 and n, the number of granules per unit volume or concentration of granules at two planes separated by a finite distance h. The resulting expression is—

$$\tfrac{2}{3}W \log \frac{n_0}{n} = \phi(D - \delta)gh.$$

Further, since W is identical with w, the mean molecular kinetic energy W may be written $\frac{3}{2}\frac{RT}{N}$, and hence the above expression may be transformed into—

$$2{\cdot}303 \frac{RT}{N} \log_{10} \frac{n_0}{n} = \tfrac{4}{3}\pi r^3 g(D - \delta)h \quad . \quad . \quad . \quad (5)$$

where $2{\cdot}303$ is the factor which reduces natural to common logs, and r is the radius of a granule.

It follows, therefore, that if we can measure the number of granules present at various heights in an emulsion and apply the above equation, we can calculate N, the "Avogadro Constant". Perrin employed emulsions of gamboge, mastic, and rubber latex. The emulsion granules were made uniform in size by centrifuging. The density D of the granules was obtained, first, by measuring the density of the substance in the massive or "solid" form, and, secondly, by determining the actual density of an emulsion, evaporating to dryness and weighing the quantity of gamboge, etc. The results of the two methods were concordant. The measurements of h and n were carried out within the limits of a microscope slide, having a small cavity, such as is used for counting the number of blood corpuscles. The microscope (Fig. 3) was focussed at different depths of the emulsion, and the average number[1] of particles in the field of view at each level noted (*cf.* Fig. 4). By carrying out an immense number of determinations Perrin succeeded in determining *n* and *h* very accurately. For details the monograph already cited should be consulted. The only other quantity to be mentioned is the size of the granules. The first method employed by Perrin is simply the method of Sir J. J. Thomson for counting the number of electrically charged particles in an ionised gas, namely, by observing the rate of fall of a cloud of particles under the action of gravity. Stokes has shown that when a particle moving at a steady rate through a medium of viscosity η encounters a frictional resistance the magnitude of the force causing the motion is given by the expression $6\pi\eta rv$, where r is the radius of the particle (assumed to be large compared with the molecular structure of the medium through which the particle passes), and v is the steady rate of motion. If gravity is the cause of the motion, the gravitational force acting on a falling granule is $\frac{4}{3}\pi r^3(D - \delta)g$, and we can equate the two expressions—[2]

$$6\pi\eta rv = \tfrac{4}{3}\pi r^3(D - \delta)g$$

from which r can be calculated.

Perrin used a capillary tube (so as to avoid convection currents), and after shaking the emulsion so that it was at uniform concentration throughout, the rate was observed at which the emulsion cleared at the top; that is, the rate of descent of the upper layers, which of course at this stage were not in the equilibrium state of distribution previously considered in the deduction of the expression for N. The only doubtful point is whether Stokes' Law holds for particles as small as these granules, the diameter of which is approximately 2 x 10^{-5} cm. As a matter of fact, as will be shown later in connection with Millikan's determination of the charge on an electron, Stokes' Law is nearly but not quite correct. The agreement obtained, however, between the method just described and a modification about to be mentioned affords confirmation of the general validity of the Stokes expression even for particles of these dimensions. The modification depends on the observation that if the liquid be made first faintly acid, then when a granule comes near the wall of the cell it sticks, although the granules in the bulk of the liquid are still in rapid motion. By this means it is possible to remove all the granules from solution and count them, thereby allowing a calculation to be made of the *average* number of granules per cubic centimetre throughout the emulsion. If the total mass of gamboge

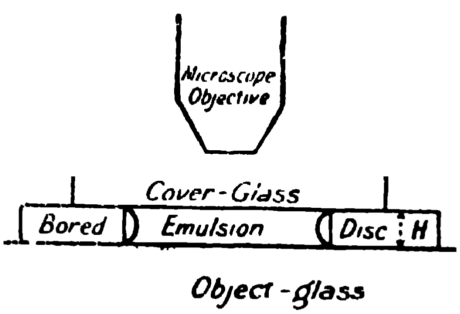


FIG. 3.

---

[1] On the basis of the law of distribution of particles with height employed by Perrin, it follows that at a depth of a few cms. the concentration would be enormous and consequently at complete variance with experiment. This criticism is made by Burton (*Proc. Roy. Soc.*, A, **100**, 1922). This criticism is confirmed and extended by Porter and Hedges (*Trans. Faraday Soc.*, **18**, 1922) who point out that "Perrin's observations are confined to very small ranges near the top of the suspensoid where the concentration was very small in order that his theoretical and experimental work might correspond to one another." Porter and Hedges show that the distribution tends to uniformity as the depth increases. Perrin's expression only holds through a layer at the surface the thickness of which is less than 0·1 mm.

[2] In this connection, see Einstein's treatment of movement of particles in a viscous medium given on p. 23.

is known, it is easy to calculate the volume of each granule, and therefore the radius, *r*.

Perrin carried out five series of experiments with gamboge emulsions, each experiment necessitating the counting of several thousand granules. The mean value for N obtained by the aid of the equation (5) was 69×10^{22}, a number which agrees sufficiently closely with the approximate values of N already referred to to justify the conclusions of Gouy regarding the cause of Brownian Movement. With mastic emulsions Perrin found $N = 70{\cdot}0 \times 10^{22}$, and finally, as a result of further series of experiments with gamboge carried out with great care, Perrin obtained the value $70{\cdot}5 \times 10^{22}$.

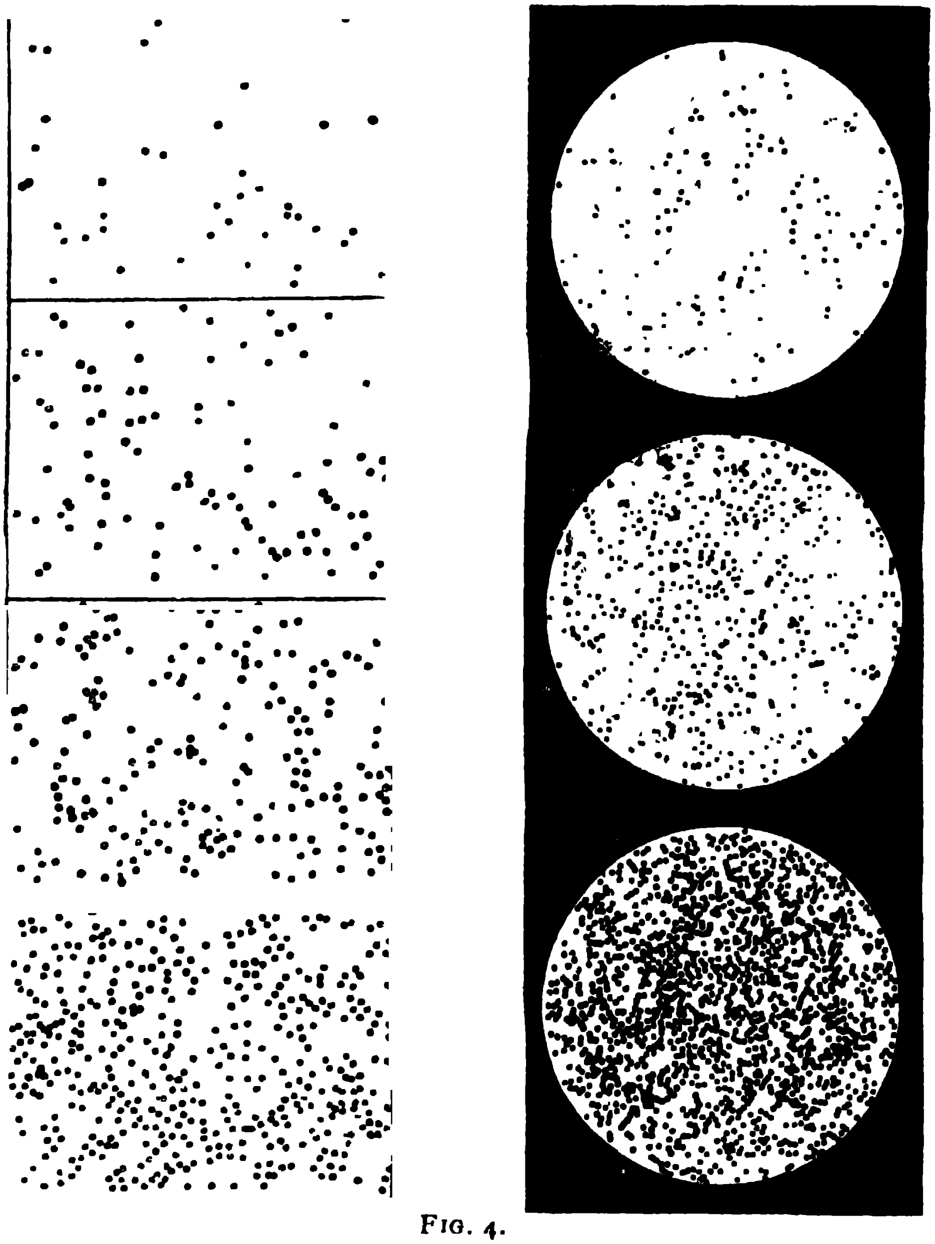


FIG. 4.

PERRIN'S SECOND METHOD.

This method is based upon theoretical considerations first put forward by A. Einstein (*Ann. der Physik* [4], **17**, 549, 1905; *ibid.* [4], **19**, 371, 1906). Einstein does not consider the concentration distribution of granules in different layers, but fixes attention upon the trajectory of a single granule along one axis—say the x axis—in one plane (xy). The actual path traversed would be quite impossible to follow, and therefore Einstein considers only the mean *rectilinear* displacement during a given time, the displacement being defined as the length of the straight line *measured as along the x axis*, which joins the point of departure to the point of arrival. In actual observations—taking a time interval of, say, 30 seconds—the displacements vary considerably from one another, but by taking a sufficient number of observations it is possible to estimate the *mean displacement* Δ with considerable accuracy. As Perrin succeeded in determining N by this means with even greater accuracy than by the first method, it is of interest to follow Einstein's mode of treatment. In the following it is given practically in Einstein's own words.[1]

EINSTEIN'S THEORY OF DIFFUSION AS APPLIED TO BROWNIAN MOVEMENT.

Diffusion and Osmotic Pressure.—Suppose the cylindrical vessel z filled with a dilute solution (Fig. 5). The internal space is divided into two parts by means of a semi-permeable movable piston, the piston being entirely permeable to the solvent but impermeable to the solute. If the concentration of solute in A is greater than that in B, there will be a force exerted upon the piston tending to move it towards the right. This force, reckoned per unit area of the piston, will be denoted by K. K evidently is the difference of the osmotic pressures exerted by the solute on the two sides of the piston. If no external force be applied, the piston will move towards the right until the concentrations in both compartments become identical. It follows therefore that osmotic pressure is the agency causing diffusion until equi-concentration is reached; for we can prevent this state being reached by balancing the osmotic pressure difference K by means of an external force applied to the piston. Suppose now that there is no piston in the cylinder, but

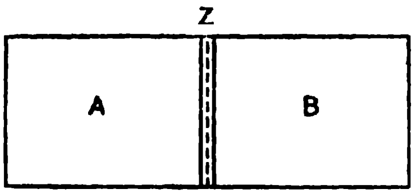


FIG. 5.

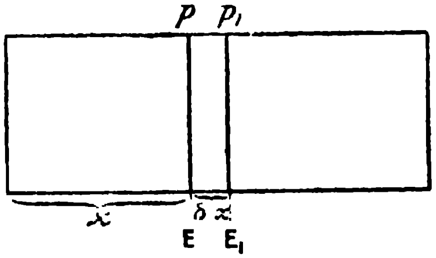


FIG. 6.

---

[1] The section which follows is a translation (with certain changes) of a paper by Einstein in the *Zeitsch. für Elektrochem.*, 14, 235-239, 1908, entitled "Elementary Theory of the Brownian Movement". The more rigid mathematical treatment is given in the *Annalen* papers referred to.

that the concentration on the left-hand side is greater than on the right, then diffusion of the solute will take place from left to right. Consider the case depicted in Fig. 6. From the left the osmotic pressure p acts on the surface E, on the right the pressure p_1 acts on the surface E_1. The resulting pressure is $p - p_1$. Let x be the distance of E from the left-hand end of the cylinder, $x + \delta x$ the distance of E_1 from the same end, the distance between E and E_1 being δx. Since $p - p_1$ is the osmotic pressure which acts on the volume δx occupied by the solute, it follows that the osmotic pressure difference reckoned per *unit* volume is

$$\frac{p - p_1}{\delta x} = - \frac{p_1 - p}{\delta x} = - \frac{dp}{dx}$$

which we shall represent by the symbol K_0. Since further the osmotic pressure is given by the equation—

$$p = RT\nu$$

where R is the gas constant ($8{\cdot}31 \times 10^7$ c.g.s. units), T the absolute temperature, and ν the number of grammoles of solute per unit volume of solution in the region E, we obtain for the osmotic pressure difference reckoned per unit volume the expression—

$$K_0 = - RT\frac{d\nu}{dx} \quad . \quad . \quad . \quad . \quad (6)$$

In order to calculate the *rate* of diffusion, one must know how great is the resistance offered by the solvent to the diffusion process. If in general a driving force k acts on a molecule, the resulting velocity v will be given by the equation—

$$v = \frac{k}{C} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where C is a constant which we might call the frictional resistance of the molecule. If we assume that a dissolved molecule is spherical, and likewise large compared to a molecule of solvent, then we have the expression $C = 6\pi\eta r$ (Stokes' expression), where η is the viscosity of the solvent and r the radius of the molecule of the solute. It may be observed that the assumption made regarding the relative size of solute and solvent molecules would be in all probability incorrect in the case of "true" solutions. In the case of emulsions and colloidal solutions, however, the work of Perrin has shown that the expression holds fairly well. It will be observed that we are making no sharp distinction between pseudo-solutions, *i.e.* emulsions and colloids, and "true" solutions.

We can now calculate the quantity of solute which diffuses through unit cross-sectional area of the cylinder in unit time. In the unit volume there are ν grammoles, that is, νN actual molecules, if N is the actual number of molecules in one grammole of gas or dissolved substance. If, therefore, K_0 divides itself over these νN molecules contained in unit volume, it follows that K_0 will give to these a velocity which would be the $\frac{1}{\nu N}$th part of that which it would give to a single molecule if it were exerted on this alone. One obtains, therefore, from equation (7) for the velocity which the force K_0 can impress on νN particles the expression—

$$v = \frac{1}{\nu N} \cdot \frac{K_0}{C}.$$

In the case which we have been considering K_0 represents difference of osmotic pressure reckoned per unit volume, so that on introducing equation (6) one obtains—

$$v\nu = -\frac{RT}{N} \cdot \frac{1}{C} \cdot \frac{d\nu}{dx}.$$

On the left-hand side stands the product of the concentration ν of the solute and the velocity with which the solute moves in the diffusion process. This product represents, therefore, the quantity of solute transported per second by diffusion through the unit cross-sectional area. This quantity divided by $-\frac{d\nu}{dx}$ is the diffusion coefficient D, where we define D as the quantity of solute transported per second through a unit cube when the concentration difference between the two ends of the cube is unity. Thus one obtains the relation—

$$D = \frac{RT}{N} \cdot \frac{1}{C} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In the special case in which the diffusing molecules are large compared with the molecules of the solvent, we can substitute Stokes' value for C, and write—

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad . \quad . \quad . \quad . \quad (8a)$$

DIFFUSION AND IRREGULAR MOVEMENTS OF MOLECULES.

The molecular theory of heat opens up a second point of view from which the process of diffusion can be considered. The irregular movements which are due to the heat content of a substance will be such that a single molecule of a gas or liquid will move about absolutely irregularly. The result of this movement in the case of dissolved molecules will be that any concentration differences initially existing in different parts of the solution will gradually vanish. Let us consider this process somewhat more closely, making the same assumptions as in the foregoing paragraphs, namely, that we restrict ourselves to the diffusion in the direction of the x axis of the cylinder. We shall consider that at a given moment t we know the x co-ordinates of all the dissolved molecules and likewise at a time $t + \tau$, where τ denotes such a short interval of time that the concentration (or rather the distribution) relations of the molecules in the solution have only altered to a slight extent. During this time τ the x co-ordinate of the first dissolved molecule will alter by a given quantity Δ_1, due to the irregular heat movements, the second molecule's co-ordinate will alter by an amount Δ_2, and so on. These displacements Δ_1, Δ_2, etc., will be partly negative (to the left), partly positive (to the right). Further, the extent of these displacements for the same molecule will vary much. But since we are considering a dilute solution, the displacements (of a solute molecule) are due to the surrounding solvent, not to any appreciable extent to the other solute molecules, and therefore the mean displacement Δ in differently concentrated solutions will be the same, and will be as often positive as negative. We have now to find out how much solute will diffuse in time τ through unit cross-sectional area when the mean magnitude Δ of the displacements is known in the direction of the x axis. To simplify the matter, the calculation will be carried out as if all the molecules experienced equal displacements Δ, one half being positive (to the right) and one half negative (to the left). Consider the state of things represented by Fig. 7. Through the plane E of a cylinder of unit sectional area during the time τ only those solute molecules will pass from left to right which initially occupied positions less distant from E than the range Δ. These molecules lie between Q_1 and E. But of these molecules only one-half have *positive* displacement, so that only one-half of them pass through the plane E. This number is $\frac{1}{2}\nu_1\Delta$, where ν_1 is the mean concentration (number per unit volume), that is, the concentration at the medium plane M_1. Since the sectional area is unity, Δ represents the volume Q_1E.

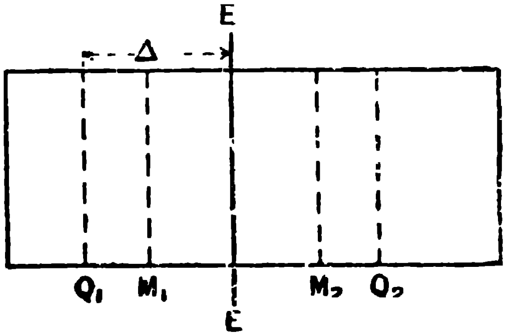


FIG. 7.

Analogous reasoning in the case of motion from right to left gives the expression $\frac{1}{2}\nu_2\Delta$, where ν_2 is the concentration at the plane M_2. The net quantity of solute which diffuses from left to right in the time τ is the difference of the two expressions, namely, $\frac{1}{2}\Delta(\nu_1 - \nu_2)$.

ν_1 and ν_2 represent the concentrations at two planes which are separated from one another by the small quantity Δ. If one denotes by x the distance of any plane from the left-hand end of the cylinder, then we can write—

$$\frac{\nu_2 - \nu_1}{\Delta} = \frac{d\nu}{dx} \text{ or } \nu_1 - \nu_2 = -\Delta\frac{d\nu}{dx}$$

so that the quantity of solute diffused through E in time τ is

$$-\frac{1}{2}\Delta^2\frac{d\nu}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The quantity in grammoles which diffuses in unit of time under the concentration gradient $\frac{dv}{dx}$ is therefore—

$$-\frac{1}{2} \cdot \frac{\Delta^2}{\tau} \cdot \frac{dv}{dx}.$$

Hence the quantity which would diffuse under unit concentration gradient (that is, when the concentrations at two different points unit distance apart differ by unity) is—

$$\frac{\frac{1}{2} \cdot \frac{\Delta^2}{\tau} \frac{dv}{dx}}{\frac{dv}{dx}} \text{ or } -\frac{1}{2} \cdot \frac{\Delta^2}{\tau}.$$

But this is simply the diffusion coefficient D.

Hence

$$D = \frac{1}{2} \cdot \frac{\Delta^2}{\tau} \quad . \quad . \quad . \qquad (10)$$

where Δ is the mean displacement[1] of any molecule along the x axis.

The Displacement of Single Molecules.

If one combines equations (8) and (10), one obtains the relation—

$$\Delta = \sqrt{\frac{2RT}{NC} \times}$$

From this formula we see that the mean displacement of a single molecule along one axis is not proportional to the time, but to the square root of the time. This arises from the fact that in two consecutive time units the distances traversed are sometimes positive, sometimes negative. In the case in which the dissolved molecule is large compared with the molecules of the solvent, and is likewise spherical, we can use equation (8*a*) in place of (8), and thus obtain the relation—

$$\Delta^2 = \tau \cdot \frac{RT}{N} \cdot \frac{1}{3\pi\eta r}.$$

This is the equation employed by Perrin in his second method of investigating the Brownian Movement, which will now be briefly described. Perrin used as before emulsions of gamboge and mastic.

In the accompanying diagram (Fig. 8) are reproduced three typical drawings of the path traced out by a mastic granule, the time intervals between each dot being 30 seconds. It is necessary to be quite clear as to how Δ^2, the mean-square-displacement of a particle along a given axis, is obtained from the observed path traced out. Suppose that L

---

[1] More accurately, Δ should be taken to be the root-mean-square displacement. Langevin, *Comptes Rendus*, 146, 530, 1908, has deduced a diffusion expression identical in form with that of Einstein.

(Fig. 9) denotes the linear distance traversed in any 30 seconds interval in the plane to which the microscope is focussed. Then $L^2 = x^2 + y^2$, and adding up numerous intervals, $\Sigma L^2 = \Sigma x^2 + \Sigma y^2$. But since the direction of the paths is quite irregular, if sufficient readings are taken,

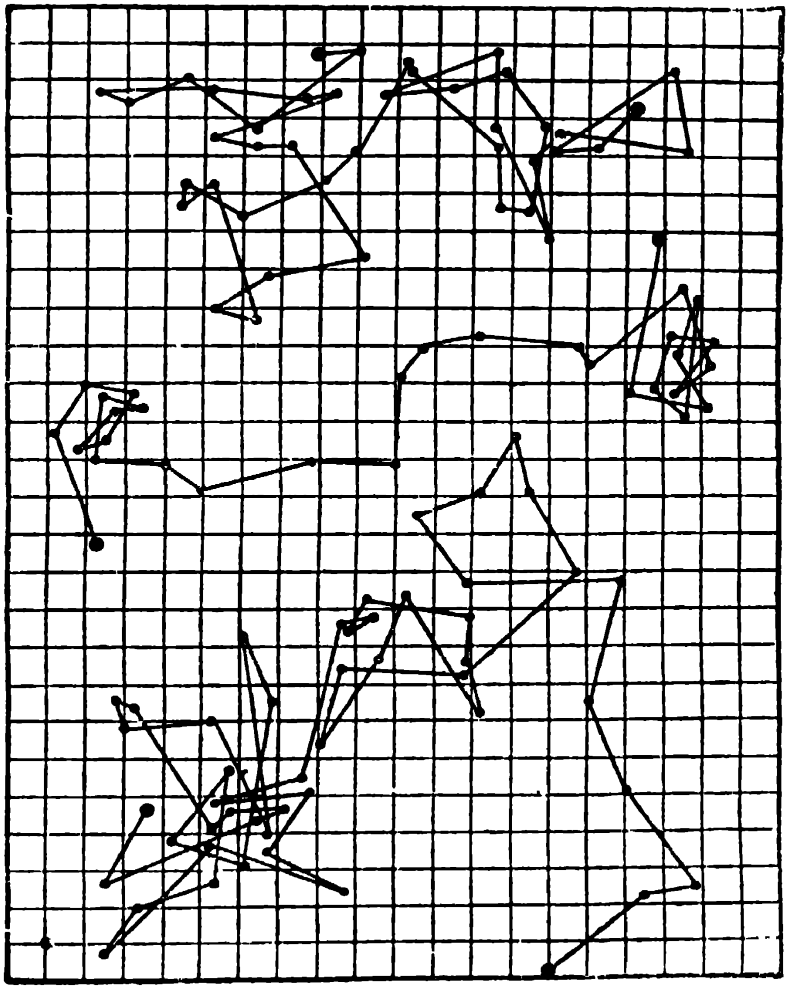


FIG. 8.

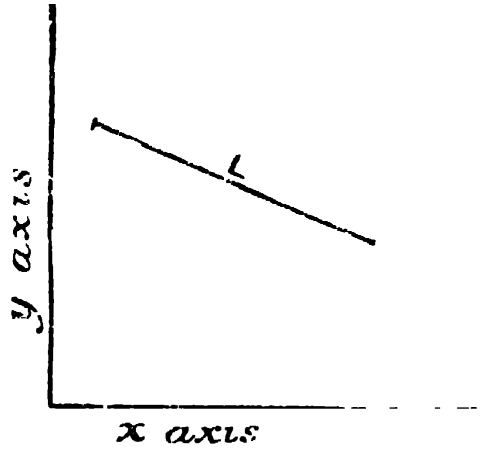


FIG. 9.

the sum of all the distances travelled by the particle along the x axis is equal to the sum along the y axis; that is $\Sigma x^2 = \Sigma y^2$, and therefore

$$\Sigma x^2 = \tfrac{1}{2}\Sigma L^2.$$

Now the mean-square-displacement Δ^2 is simply the mean of the terms denoted by Σx^2, and therefore Δ^2 is one-half of the mean square of the observed paths (L) in the horizontal plane xy.

Perrin observed several thousands of such displacements with gamboge and mastic granules, and after applying Einstein's equation, he obtained as a mean result—

$$N = 71{\cdot}5 \times 10^{22}$$

which agrees extremely well with the values obtained by the first method.[1] Recently Perrin (*Comptes Rendus*, **152**, 1380, 1911) has repeated his experiments, using resin emulsions. The method of measuring the equilibrium concentration distribution at different levels led to the value $68{\cdot}3 \times 10^{22}$. The method depending upon Einstein's equation led to the value $68{\cdot}6 \times 10^{22}$. The most accurate mean value up to the present is, according to Perrin—

$$N = 68{\cdot}5 \times 10^{22}.$$

Reference will be made later to other determinations of N in discussing the question of the charge on an electron.

SVEDBERG'S INVESTIGATIONS UPON THE APPLICABILITY OF BOYLE'S LAW TO COLLOIDAL SOLUTIONS. (See *Zeitschr. physik. Chem.*, **73**, 547, 1910; *ibid.*, **77**, 145, 1911.)

The work carried out within recent years by Theodor Svedberg in connection with the osmotic pressure of colloidal solutions,[2] is based on certain relationships deduced by von Schmoluchowski (Boltzmann Festschrift, *Annalen der Physik*, p. 626, 1904; *ibid.* [4], **25**, 205, 1908), in which the compressibility β_0 of a perfect gas is connected with the compressibility β of a non-perfect gas in terms which are measurable in the case of a colloidal solution, the latter being at first sight a very extreme case indeed of a non-perfect gas. Svedberg determined the ratio $\frac{\beta}{\beta_0}$. If the gas law applied accurately to the particles of a colloidal solution the ratio should be unity. Working with dilute colloidal solutions Svedberg obtained for the ratio a mean value very nearly unity, a few of the actual values (chosen practically at random) being 0·903, 0·981, 0·988, 1·00, 1·013, 1·029. These results support in a very conclusive manner the kinetic treatment of the behaviour of particles in colloidal solution.

---

[1] Perrin also verified another equation deduced by Einstein involving a measurement of the *rotation* of the granules, but as this is much more difficult to observe, the results are presumably less accurate.

[2] Colloidal solutions are discussed in Vol. I., Chap. VIII.

THE ELECTRICAL CHARGE ON A MONOVALENT ELECTROLYTIC ION.

It is known that one faraday of electricity, or 96,540 coulombs, is required for the deposition from solution of one gram equivalent of any ion (or charged atom). If we have a solution containing one grammole of hydrochloric acid and electrolyse it completely, evidently the number of hydrogen ions discharged at the cathode will be identical with the number of molecules of hydrochloric acid originally present in the solution,[1] that is, $68 \cdot 5 \times 10^{22}$. Hence the charge on a single hydrogen ion is $\frac{96540}{68 \cdot 5 \times 10^{22}}$ coulombs, or $4 \cdot 19 \times 10^{-10}$ electrostatic units. [One coulomb is $\frac{1}{10}$ of one electromagnetic unit, and one electromagnetic unit is 3×10^{10} electrostatic units.]

We shall see later that the charge on a monovalent electrolytic ion is identical with that on an electron—that is, identical in magnitude though not necessarily in sign, since electrons are negatively charged, while cations are positively charged, and anions negatively. The most accurate value yet obtained for the charge on a monovalent ion is $4 \cdot 77 \times 10^{-10}$ electrostatic units (*vide infra*).

THE CONSTITUTION OF MOLECULES AND ATOMS.

We can obtain some information of a more or less qualitative nature respecting the differences in constitution of the molecules of various gases from considerations of the specific heat of the gas. A gas possesses two specific heats; first, the specific heat at constant volume, denoted by C_v, which represents the amount of heat which has to be added to one gram of the gas to raise its temperature one degree, the volume of the gas being kept constant; and secondly, the specific heat at constant pressure, denoted by the symbol C_p, which represents the amount of heat required to raise one gram one degree, the volume being allowed to expand at constant pressure. In the latter case the gas does *work* against the atmosphere, the amount of such work being represented by the product of the pressure into the increase in volume. As we shall see in dealing with the principles of thermodynamics (Chap. I., Vol. II.), this work must be done at the expense of some of the heat added, and therefore it requires more heat to be added to raise the temperature of the gas at constant pressure than it does at constant volume. We have now to find an expression for the difference of the two specific heats; that is, the heat equivalent of the work done by expansion. Consider one gram of gas at volume v, temperature T, and pressure p. The relation between these quantities is $pv = RT$, where R has in this instance the numerical value $\frac{1 \cdot 985 \text{ calories}}{\text{molecular weight of the gas}}$. Again consider the same mass of gas at the temperature $(T + 1)$, the pressure being p as before, but the volume is now greater, namely, v_1. Again the relation $pv_1 = R(T + 1)$ must hold. Subtracting the two equations one finds $p(v_1 - v) = R$. But $p(v_1 - v)$ is the work done[1] in the expansion at constant pressure during the heating-up process. Hence the work done is R heat units, and this must be the difference of the two specific heats, that is—

---

[1] **Reckoned, of course, as though there had been *no* electrolytic dissociation of the HCl to start with.**

$$C_p - C_v = R.$$

Hence the gas equation can be written in general—

$$pv = (C_p - C_v)T.$$

Also, we saw on the basis of the kinetic theory that—

$$pv = \tfrac{1}{3}u^2 \text{ (for a mass of 1 gram)}$$

and therefore $u^2 = 3(C_p - C_v)T$.

Further, since the expression for the kinetic energy of translation of a molecule is $\frac{1}{2}mu^2$, it follows that the total kinetic energy of translation of one gram is $\frac{1}{2}u^2$. Besides this energy of translation there is also internal energy in the molecules themselves due to internal vibrations, rotations of atoms round one another, etc. Let us make the assumption[2] that this internal energy is proportional to the energy of translation, that is, is given by the expression $K\frac{1}{2}u^2$, where K is a constant. Hence the total energy of all sorts in one gram of gas at a temperature T is—

$$\tfrac{1}{2}(1 + K)u^2$$

which is equal to—

$$\tfrac{3}{2}(C_p - C_v)(1 + K)T.$$

Now if heat be added to the gas so as to raise its temperature one degree, the volume being kept constant, *i.e.* no external work being done, then all the heat added goes to increase the energy of the molecules. This increase is simply the specific heat at constant volume C_v, and is likewise the difference between the total energy at (T + 1) and the total energy at T. That is—

$$\begin{aligned} C_v &= \tfrac{3}{2}(C_p - C_v)(1 + K)(T + 1) - \tfrac{3}{2}(C_p - C_v)(1 + K)T \\ &= \tfrac{3}{2}(C_p - C_v)(1 + K). \end{aligned}$$

Further, if we put the ratio $\frac{C_p}{C_v}$ equal to γ, then the above equation may be transformed into—

$$\gamma = 1 + \frac{2}{3(1 + K)}.$$

Since we may expect K to be *in general* a positive quantity, this relation shows that—

$$\gamma < 1\tfrac{2}{3} \text{ or } 1{\cdot}666.$$

---

[1] See Chap. I., Vol. II.

[2] This is simply an attempt to avoid introducing at this stage the Boltzmann theory of the equipartition of energy among the different "degrees of freedom" of the molecule. This is discussed later and more fully in Vol. III.

In the particular case of monatomic gases (the rare gases and metallic vapours) the internal rotation of atoms with respect to one another is impossible, so that putting K = 0 we obtain for this case—

$$\gamma = 1{\cdot}666.$$

These conclusions may be tested by direct measurements of specific heats, from which one obtains values for γ. In the following table the values for γ for a few gases are given:—

	γ.
Mercury vapour, Hg	1·666
Nitrogen, N_2	1·410
Ammonia, NH_3	1·30
Methyl ether, $(CH_3)_2O$	1·113
Ethyl ether, $(C_2H_5)_2O$	1·029[1]

With increasing complexity of the molecule K necessarily increases in magnitude, with the result that γ decreases.

We cannot learn more about molecular constitution from the study of specific heats unless we introduce the principles which belong to "statistical mechanics" (*cf.* Vol. III.). We shall here only indicate the meaning of the term "degrees of freedom" of a molecule.

A degree of freedom is defined as an independent mode in which a body may be displaced. To find out the number of degrees of freedom possessed by a body or system let us consider a simple case, namely, a single rigid body in space, say a solid sphere. The centre of gravity of the body is free to move parallel to any of the three space co-ordinates X, Y, Z. That is to say, as far as *translation* is concerned, a body, free to move in space, possesses *three* degrees of freedom. But such a body is likewise capable of *rotation*. It may rotate about three axes parallel to XYZ. (All other rotations can be resolved into component rotations about each of these three axes.) On the whole, therefore, a body such as we have been considering possesses *six* degrees of freedom. If a body possesses a "constitution" of some kind, that is, is made up of various portions, each of which may rotate or vibrate with respect to one another, the number of degrees of freedom of the body is correspondingly increased, and to estimate the actual number of degrees of freedom soon becomes impossible. The important generalisation connected with degrees of freedom, and known as Boltzmann's "theorem of the equipartition of energy" between the different degrees of freedom possessed by a body, may be stated thus: the total kinetic energy of a system (due to translation, rotation, vibration, etc.) is *equally* divided up between all the degrees of freedom, and it can be shown that the amount of energy per degree of freedom amounts to $\frac{1}{2}$RT, the unit of mass being the grammole. This theorem has been much criticised, but it would be altogether beyond our purpose to attempt to follow it. The application of the theorem in connection with the heat content of solids is discussed in Vol. III.

---

[1] Ether has been investigated in a very complete manner by Perman, Ramsay, and Rose-Innes (*Zeitschr. physik. Chem.*, 23, 385, 1897), values of γ being directly calculable from the observed velocity of sound measured both for the vapour and liquid over a wide temperature and pressure range.

Although we have not been able to infer much regarding constitution from specific heat, a more successful attack has been made upon the problem from the standpoint of "electrons" or "corpuscles," of which, according to Sir J. J. Thomson, electricity—negative electricity—itself consists.

SOME APPLICATIONS OF THE CORPUSCULAR OR ELECTRON THEORY TO THE PROBLEM OF MOLECULAR AND ATOMIC CONSTITUTION.

According to this theory, negative electricity consists of extremely small particles called corpuscles or electrons, which are all identical in size, and carry the same charge. These corpuscles are much smaller than atoms, and according to the theory, atoms, and therefore molecules, are partly built up of corpuscles. Of course to prevent spontaneous disintegration of the atom due to the mutual repulsion of a number of similarly charged electrons, it is necessary to assume the existence of an equal amount of positive electricity. It is assumed, therefore, that a neutral atom consists of a sphere of positive electricity (J. J. Thomson) which contains a number of corpuscles moving in various orbits, the number of such corpuscles and the kind of motion they possess being the ultimate source of chemical and physical "properties". It will be of interest to consider briefly the experimental evidence in favour of the real existence of corpuscles.

Corpuscles were first discovered during the electrical discharge through a highly exhausted tube. Rays are shot off from the cathode, and these may be stopped by the interposition of some material placed in their path. These cathode rays, as they are called, on striking the walls of the tube cause a vivid green fluorescence upon soda glass, blue on potash glass. That these rays consist of negatively charged particles was shown by the fact that they can be deflected in certain directions by a magnetic or an electrostatic field, or both simultaneously. The first important quantity which would serve to characterise these rays is the ratio of their mass to their charge. To obtain this we have to consider the effects produced by a magnetic and an electrostatic field upon the direction of motion of the particles. Suppose that a single corpuscle mass m carrying a charge e is moving with a velocity v cms. per second through the tube, then by putting on a magnetic field of strength H it is possible to deflect the course of the corpuscle in a given direction. If simultaneously an electrostatic field be set up (by connecting two parallel pieces of metal placed inside the tube to the two ends of a battery) in such a direction that it just compensates the effect of the magnetic field so that the path of the corpuscle is undeflected, then we can equate the effect due to the magnetic field to that due to the electrostatic. The magnetic force acting amounts to Hev, and if X is the strength of the electrostatic field the electrostatic force exerted upon the electron is Xe, so that when these two forces just balance we have—

$$Hev = Xe$$

or

$$v = \frac{X}{H}.$$

By means of this equation one can determine the velocity of the cathode rays. In a highly exhausted tube this may attain to a velocity approximately one-third of the velocity of light, that is to say, about 60,000 miles per second. This is many thousand times the velocity of a hydrogen molecule at ordinary temperature, or indeed at any temperature yet realised.

Now let us suppose that the magnetic field is removed. The corpuscles are acted upon by the electrostatic field, which causes their path to be deflected. The behaviour is analogous to that of a bullet travelling horizontally at a high speed, and at the same time falling towards the earth owing to gravitation. We know that in the time t the bullet will fall by the amount $\frac{1}{2}gt^2$, where g is the acceleration of gravity. In the case of the corpuscle, since the downward force (supposing it to act downwards) is Xe, and since, in general, force = mass × acceleration, or acceleration $= \frac{\text{force}}{\text{mass}}$, it follows that if m is the mass of a corpuscle, the downward acceleration is $\frac{Xe}{m}$, and the distance through which it falls in time t is $\frac{1}{2}\frac{Xet^2}{m}$. If l is the horizontal distance travelled with velocity v during the time t, then $t = \frac{l}{v}$. Hence the vertical distance over which the particle falls (which is measured by observing the vertical displacement of the phosphorescent spot on the glass) is given by the expression

$$\frac{1}{2} \cdot \frac{Xe}{m} \cdot \frac{l^2}{v^2}.$$

Now we can measure d, the vertical displacement of the phosphorescent spot, and as we already know v, X, and l, it is possible to calculate the ratio $\frac{e}{m}$ from the equation—

$$\frac{e}{m} = \frac{2d}{X} \cdot \frac{v^2}{l^2}.$$

In this manner it has been found that the ratio $\frac{e}{m}$ is the same for all cathode rays provided they are not moving with a velocity approaching the velocity of light. Further, this ratio is independent of the chemical nature of the electrodes, and likewise of the nature of the gas which still remains in the tube. The value for $\frac{e}{m}$ on the c.g.s. system electromagnetic units is $1{\cdot}772 \times 10^7$. Prior to the examination of the cathode rays the largest known value for the ratio of the charge to the mass was met with in the case of the hydrogen ion in aqueous solution. The most recent value for the charge on such an ion is $4{\cdot}77 \times 10^{-10}$ electrostatic units, and the mass of one hydrogen atom or ion is $1{\cdot}64 \times 10^{-24}$ gram (*vide infra*), so that in this case the ratio of charge to mass is $2{\cdot}9 \times 10^{14}$. To convert this into electromagnetic units it is necessary to divide by the factor 3×10^{10}, so that the ratio $\frac{e}{m}$ for the hydrogen ion is $0{\cdot}97 \times 10^4$. The ratio $\frac{e}{m}$ for a single particle of the cathode rays is therefore $\frac{1{\cdot}772 \times 10^7}{0{\cdot}97 \times 10^4}$ times, or 1830 times greater than the ratio $\frac{e}{m}$ for the hydrogen ion. This must arise in one of two ways; first, either the charge on the corpuscle is 1830 times greater than the charge on the hydrogen ion, the mass of the ion and the corpuscle being assumed identical, or, secondly, the charges may be identical but the mass of the corpuscle only $\frac{1}{1830}$ of that of the hydrogen ion. To settle which of these alternatives is the correct one it is necessary to determine the charge *e* on a single corpuscle.[1]

MAGNITUDE OF THE CHARGE ON AN ELECTRON OR CORPUSCLE.

To determine this quantity use is made of the discovery of C. T. R. Wilson that if electrically charged particles are introduced into a vessel containing supersaturated vapour—say water vapour—condensation of the vapour will occur upon the charged particles, which act as nuclei for the droplets of the cloud which falls slowly under the action of gravity. The experiment is easily carried out if a source of X rays or if some radium salt be brought near the vessel, since the rays shot off by the radium salt penetrate the walls of the vessel and ionise the gas inside, thereby producing a number of positively and negatively electrified particles which act as nuclei. The negative particles are simply atoms which have gained an electron, the positives being the charged atomic "residues" left after the removal of an electron from the neutral atom. C. T. R. Wilson has shown that condensation takes place more easily upon the negative particles than upon the positive ones, and it is possible, as was shown by H. A. Wilson, to so adjust the degree of supersaturation that condensation takes places *only* upon the negative ones. The rate v at which the cloud falls is given, according to Stokes, by the expression—

---

[1] For a fuller discussion of the method of obtaining the ratio $\frac{e}{m}$ for the corpuscle the reader is referred to Sir J. J. Thomson's *Electricity and Matter* or *The Corpuscular Theory of Matter.* An "Elementary treatment of the motion of a charged particle in a combined electric and magnetic field," is given by W. B. Morton, *Proc. Physical Soc.*, **21**, 300, 1908.

$$v = \frac{2}{9} \cdot \frac{gr^2\rho}{\eta}$$

where g is the acceleration of gravity, η the viscosity of the gas, ρ the density of the droplet, and r the radius of one of the droplets. It is thus possible to determine r, and therefore the volume of each droplet. We can also determine the total volume of water condensed when we know the extent of supersaturation, which in turn can be obtained if we know the dimensions of the vessel and the travel of the piston fitted into the vessel—the piston being employed to bring about the state of supersaturation in the vessel which contains air and unsaturated water vapour. It is therefore possible to calculate the total number of droplets in the cloud. Now it is easy to measure the total charge on the cloud by measuring the ionisation current which occurs when a certain potential difference is applied to the ionised gas. We can thus obtain the charge on each droplet, and assuming that each droplet is condensed on a nucleus having a single charge e, we have at once the charge carried by an electron.

An alternative mode of procedure was adopted by H. A. Wilson, who observed the rate of fall of the cloud under gravity alone and then under the simultaneous action of gravity and a known electrostatic field. If v_1 denotes the velocity of fall under gravity alone, and v_2 the velocity under gravity plus an electric force Xe, where X is the strength of the field or the potential gradient, then we have the relation—

$$\frac{v_1}{v_2} = \frac{mg}{mg + \mathrm{X}e}.$$

Introducing Stokes' expression for v_1, namely—

$$v_1 = \frac{2}{9} \cdot \frac{gr^2\rho}{\eta}$$

where ρ is the density of a droplet and $m = \frac{4}{3}\pi r^3\rho$, we obtain, on combining the above equations, the expression—

$$e = \left\{\frac{4}{3}\pi\left(\frac{9\eta}{2g}\right)^{\frac{3}{2}}\right\}\frac{g}{\mathrm{X}} \frac{(v_2 - v_1)v_1^{\frac{1}{2}}}{\rho^{\frac{1}{2}}} \quad . \quad . \quad . \quad (11)$$

By the aid of the above and other modifications, it was found that $e = 3{\cdot}1 \times 10^{-10}$ electrostatic units, or 1×10^{-20} electromagnetic c.g.s. units. Now we have seen that the charge on a hydrogen ion is $4{\cdot}19 \times 10^{-10}$ electrostatic units, so that within the limits of experimental error (which in the earlier determinations such as the one given were fairly wide), we are justified in concluding that *the charge* e *upon a corpuscle is identical with that on a monovalent electrolytic ion.* But the ratio of $\frac{e}{m}$ for the corpuscle is 1830 times that for the ion; we must therefore conclude that the mass of the ion or atom is 1830 times greater than that of the corpuscle.

The above value for e is, however, not a very accurate one. It has been redetermined recently by Millikan with great care. The results are briefly as follows :—

MILLIKAN'S DETERMINATION OF "e" BY A MODIFICATION OF THE WILSON CLOUD METHOD. (See Millikan, *Phil. Mag.* [6], **19**, 209, 1910.)

Millikan attempted to obtain a sufficiently strong electric field to exactly *balance* the force of gravity upon the cloud of charged droplets. It was found that this could only be partially realised, but instead Millikan succeeded in holding *individual charged drops* suspended in the field from 30 to 60 seconds. The droplets which it was possible to thus suspend always contained multiple charges ($2e$ to $6e$). The procedure is simply to form a cloud as previously described, the source of the ionisation employed by Millikan being a radium salt. The electric field is then excited. The drops which have charges of the same sign as that of the upper plate or too weak charges of the opposite sign, rapidly fall, while those which are charged with too many multiples of sign opposite to that of the upper plate are jerked up against gravity to this plate. The result is that after a lapse of six or eight seconds the field of view in the observation telescope has become quite clear save for a relatively small number of drops which have just the right ratio of charge to mass to be held suspended by the electric field. The observations were made by means of a telescope having three equally spaced horizontal hairs in the eyepiece, the distance between the extreme hairs being about one-third of the distance between the two charged plates producing the electric field. The cross hairs were set near to the lower plate (the electric field being on), and as soon as a stationary droplet was found somewhere above the upper cross hair, it was watched for a few seconds to make sure it was not moving, *i.e.* falling or rising, and then the electric field was thrown off. The drop was then timed in its fall under gravity as it passed across the three hairs. This method affords a check on any evaporation of the drop, if such occurs, since in this event the rate of travel between the first and second hair would be faster than that between the second and third.[1] In general the times taken were the same. We can apply equation (11), remembering that in the balanced state, $v_2 = 0$ and X is negative in sign (since it opposes gravity). We thus obtain the relation—

$$e = 3{\cdot}422 \times 10^{-9} \frac{g}{X}(v_1)^{\frac{3}{2}}.$$

---

[1] **Remember that we are supposed to be considering the motion of a droplet which is moving at a *steady* rate, the *acceleration* due to gravity being balanced by the frictional resistance of the medium.**

Millikan carried out a large series of determinations of e by this method, the extreme values being $4{\cdot}87 \times 10^{-10}$ and $4{\cdot}56 \times 10^{-10}$. The mean value adopted is $e = 4{\cdot}65 \times 10^{-10}$ *electrostatic units.* For the purpose of comparison, attention may be drawn to the following alternative values of e obtained by different methods:—

1. Planck calculated $e = 4{\cdot}69 \times 10^{-10}$, using Kurlbaum's radiant energy data (see Vol. III.).

2. Rutherford and Geiger (*Proc. Roy. Soc.*, A, **81**, 141, 161, 1908) obtained $4{\cdot}65 \times 10^{-10}$ by counting the number of α particles emitted by a known quantity of radium salt and measuring the total electrical charge carried by these particles.

3. Regener's value $4{\cdot}79 \times 10^{-10}$ (*Sitzungsbericht d. k. preuss. Akad.*, **38**, 948, 1909), obtained by counting the number of scintillations produced by a known amount of polonium and measuring the total charge carried.

4. Begeman obtained $e = 4{\cdot}67 \times 10^{-10}$ as a mean of a large number of measurements carried out by the Wilson method.

Millikan does not consider Perrin's value of N (which, as already pointed out, leads to a value for e) as sufficiently accurate.[1] The most probable value for e obtained up to the year 1910 is, according to Millikan, $4{\cdot}69 \times 10^{-10}$ electrostatic units. Using this number, he has calculated N to be $61{\cdot}8 \times 10^{22}$ and the number of molecules per cubic centimetre of a gas at normal temperature and pressure to be $2{\cdot}76 \times 10^{19}$. The mass of one hydrogen atom is also easily calculable and comes out to be $1{\cdot}62 \times 10^{-24}$ gram.

MILLIKAN'S "OIL DROP" METHOD OF DETERMINING THE CHARGE ON AN ELECTRON. (Millikan, *Physical Review*, **32**, 349, 1911. For a summary of the method and the results obtained, see Millikan, *Trans. Amer. Electrochem. Soc.*, **21**, 185, 1912.)

The following brief account is given partly in Millikan's own words.

An apparatus was set up consisting of two metal plates, separated by an air layer across which a known potential difference of several thousand volts could be thrown. The upper plate was pierced about its centre with a small pinhole, thereby communicating to a large air chamber above into which a very fine spray of oil droplets could be pumped. The air between the plates was ionised by means of X rays, thereby giving rise to an equal number of positive and negative gaseous "ions". An oil drop on passing through the pinhole entered the region of ionised air, and ultimately caught one or more of the ions. Even before entering this region the oil drop was electrically charged (by friction in the spraying process), and hence it could be made to move up or down in the field of view, according as the electrical field was thrown on or off. On catching an ion the rate at which the drop was moving upward in the electrical field was observed to change abruptly, and by measuring the velocity of the same drop over an extended series of time intervals, the number of charges communicated to it could be obtained. The precision of the measurements and the certainty with which the unitary or discrete nature of electricity follows as a result of the measurements can best be appreciated by inserting the results of a single experiment. Column I. gives the successive times in seconds taken by the droplet in falling under the action of gravity alone between two fixed cross hairs in the eyepiece of the telescope, the actual distance of fall being 0·5222 cm. It will be seen that these numbers are exceedingly concordant. Column II. gives the successive times which the same droplet required to rise the same distance under the influence of the electrical field, when a potential of 5051 volts was applied.

---

[1] Perrin has, however, replied to Millikan's criticism. See *Phil. Mag.*, **19**, 438, 1910.

Column I.	Column II.
13·6	12·5
13·8	12·4
13·4	21·8
13·4	34·8
13·6	84·5
13·6	85·5
13·7	34·6
13·5	34·8
13·5	16·0
13·8	34·8
13·7	34·6
13·8	21·9
13·6	
13·5	
13·4	
13·8	
13·4	
Mean 13·595	

It will be seen that after the second trip up (in the electric field) the time changed from 12·4 to 21·8, indicating (since the droplet was *positively* charged by the spraying process) that a *negative* ion had been caught from the air. (If the particle had been completely discharged it would, of course, not have moved upward at all but downward, with a velocity indicated by the figures of column I.) The next recorded time in column II. is 34·8, which indicates that another negative ion has been caught. The next time period, 84·5, indicates the capture of still another negative ion. This charge was held for two trips, when the time interval changed back again to 34·6, showing that a positive ion had now been caught—(Millikan considers the loss of an electron by the droplet as unlikely)—this positive charge being precisely the same in magnitude as that of the negative ion which before caused the inverse change in the time interval, *i.e.* from 34·8 to 84·5. To find the absolute value of these charges, it is necessary to know the mass m_d of the droplet. Their *relative* magnitudes can be obtained, however, in the first instance, without determining m_d. Thus, let us consider the up and down movement separately. The downward force due to gravity is mg, the upward force due to the electrical field is Xe. Hence if v_1 is the velocity downward due to gravity, and v_2 the velocity upward due to the excess of the electrical field over the gravitational, we find—

$$\frac{v_1}{v_2} = \frac{m_d g}{Xe - m_d g} \text{ or } e = \frac{m_d g}{Xv_1}(v_1 + v_2) \quad . \quad . \quad (12)$$

Thus the charge added to the droplet at an encounter is proportional to the *change* produced in the sum of the two velocities by the capture, for m_d, g, v_1, and X are constant. Now, the change in this sum produced by the capture of the ion which caused the time interval in column II. to change from 34·8 to 84·5 was 0·00891 cm. per second,[1] and the successive values of this quantity arranged in order of magnitude were 0·04456, 0·05347, 0·06232, 0·07106, 0·08038. If now electricity is "atomic" in structure (*i.e.* consists of small units), all the different charges appearing in this experiment should be exact multiples of the elementary unit of charge, which means that all the numbers given above should be exact multiples of something. Dividing the last five numbers by 5, 6, 7, 8, and 9 respectively, one obtains the series: 0·008912, 0·008911, 0·008903, 0·008883, and 0·008931, which are all seen to be within one-fifth of 1 per cent. of the value 0·00891, which is the change in the sum of the speeds produced by the capture of the first ion. Hence the charge added to the droplet on capturing this ion is itself the elementary unit; the total charge at any moment borne by the droplet during the course of the experiment being an even multiple of this number. Nearly one thousand different drops have been examined in the manner indicated, some of them being oil (a non-conductor), some being glycerine (a semi-conductor), and some mercury (a good conductor), and in all cases the initial charge placed upon the drop by the frictional (spraying) process, and all of the dozen or more charges which resulted from the capture by the drop of a larger or smaller number of ions have been found to be exact multiples of the smallest charge caught from the air. This is the most conclusive proof of the "atomic" structure of electricity.

By means of equation (12) Millikan obtained very accurate values for $\frac{e}{m_d}$, where m_d is the mass of the droplet in this case. To obtain e it is therefore necessary to determine the mass m_d. Stokes' expression

---

[1] In the first case (time = 34·8 secs. against gravity), since the actual distance travelled is 0·5222 cm.—

$$v_1 + v_2 = \left(\frac{0·5222}{13·595} + \frac{0·5222}{34·8}\right).$$

In the second case—

$$v_1 + v_2 = \left(\frac{0·5222}{13·595} + \frac{0·5222}{84·5}\right)$$

and hence the difference is—

$$0·5222\left(\frac{1}{34·8} - \frac{1}{84·5}\right) = 0·00891 \text{ cm. per second.}$$

for the velocity of fall under gravity, namely, $v_1 = \frac{2}{9} \cdot \frac{gr^2}{\eta}$, allows of our calculating the radius, and therefore the volume and mass of the droplet—assuming the density of the droplet to be that of the oil in bulk. As a result of special experiments, however, Millikan found that the above expression was not quite accurate for this case. He therefore modified it slightly by the addition of an empirical term, and with this more accurate form calculated r, and eventually m_d. The value of e was thus directly obtained. As a mean of a very large number of values, Millikan gives the value (*British Ass. Rep.*, p. 410, 1912)—

$$e = 4{\cdot}775 \times 10^{-10} \text{ electrostatic units,}$$

the error not exceeding 1 part in 1000.

An interesting fact discovered by Millikan in experiments somewhat similar to those described, in which the droplet was held in suspension, was that only *one* electron is detached from a given gas molecule when the gas is ionised. The oil droplet was "in a veritable shower of the positive residues of the molecules split up by the rays," yet in no case did a capture of one of these residues communicate more than one electrical unitary charge. If two electrons had been ionised off a molecule, the positive residue would carry two unitary charges, and would communicate these to the droplet on collision. Since out of 500 "catches," 496 were certainly single unitary charges, the remaining four being doubtful, the conclusion is that the process of ionisation consists in the expulsion of one electron from a molecule.

THE "OIL DROP" METHOD OF STUDYING BROWNIAN MOVEMENT IN GASEOUS MEDIA.

Perrin's observations on Brownian movement refer to particles suspended in a *liquid* medium. Millikan (*l.c.*) has succeeded by his electrified oil drop method in determining the extent of the movement of the drop when balanced in air by having the electric field adjusted to the gravitational field. The arrangement is similar to that already described, the only modification being that of enclosing the apparatus in order to permit of lowering the air pressure, since the Brownian movement of the droplet only becomes measurable at low pressures. Several hundred determinations were made of the distance travelled by the droplet in a vertical direction in ten seconds, for as we have already seen Einstein's theory is developed in such a way that only movements along one axis have to be considered. The expression for the mean-square-displacement Δ^2 is—

$$\Delta^2 = \frac{2RT\tau}{NC}$$

where C is the frictional resistance of the medium. Millikan's final expression, based on a more rigid treatment[1] than that given earlier, takes the form—

$$\Delta = \sqrt{\frac{4}{\pi} \cdot \frac{RT\tau}{NC}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The essential advantage of Millikan's method lies in the elimination of C. This is done by observing the successive displacements of the *balanced* drop and then to destroy the balance and measure the rate of fall of the drop (under gravity alone) and under gravity *assisted* by the electrical field. Suppose that the drop moves down under gravity (force = $m_d g$) with a velocity v_1. We have then the relation $m_d g = Cv_1$. Substituting this value of $m_d g$ in equation (12), we obtain—

$$e = \frac{C}{X}(v_1 + v_2)$$

and combining this with equation (13) we can eliminate C, obtaining finally the relation—

$$\Delta = \sqrt{\frac{4}{\pi} \cdot \frac{RT(v_1 + v_2)\tau}{XNe}}.$$

With the help of this equation Millikan calculated the value of $\sqrt{Ne}$, which came out $1 \cdot 698 \times 10^7$ electrostatic units, this being the total quantity of current carried by one grammole of a univalent substance. Now $\sqrt{Ne}$ is known very accurately in the case of silver from measurements of the quantity of current required to precipitate one gram equivalent of silver from solution. The value is $1 \cdot 702 \times 10^7$ electrostatic units. This agreement to less than one-fourth of 1 per cent. between the values of $\sqrt{Ne}$ may be taken as proving that the value of e on the gas ions is the same as the charge on the univalent ion in solution, provided the kinetic theory of Brownian movement is assumed to be correct; or *vice versâ*, if the identity of the charge on the gaseous ion and the electrolytic ion is considered as established by the work of Townsend and others, then Millikan's experiments establish in a very rigid manner the correctness of the kinetic treatment of Brownian motion.

THE VALUE OF THE AVOGADRO CONSTANT, N.

A table summarising the various determinations of N and e up to the year 1910 is given by Burton (*Physical Properties of Colloidal Solutions*, p. 88). If we employ Millikan's value for e already quoted (*viz.* $e = 4 \cdot 775 \times 10^{-10}$ electrostatic units), and the value of $\sqrt{Ne}$ given above, we find $N = 6 \cdot 06 \times 10^{23}$. A. Westgren (*Zeitsch. anorg. Chem*, **93**, 231, 1915), using Perrin's first method, has found $N = 6 \cdot 05 \pm 0 \cdot 3 \times 10^{23}$. Schidlov (*Arch. Sci. phys. nat.*, **40**, 339, 1915) has concluded, as a result of comparing various observers' values of e, that N lies between 6·0 and $6{\cdot}2 \times 10^{23}$. The most accurate value, determined by Millikan (*Proc. Nat. Acad. Sci.*, **3**, 314, 1917; *cf.* also *Phil. Mag.* [6], **34**, 1, 1917), is $\mathbf{N} = \mathbf{6{\cdot}062} \pm 0{\cdot}006 \times \mathbf{10^{23}}$. This value depends on Millikan's most recent determination of *e*, *viz.* $\mathbf{e} = \mathbf{4{\cdot}774} \pm 0{\cdot}005 \times \mathbf{10^{-10}}$ electrostatic units. From the above value of N we can easily calculate *n*, the number of molecules in one c.c. of any gas—more or less perfect—at 0° C. and 760 mm. $\mathbf{n} = \mathbf{2{\cdot}705} \pm 0{\cdot}003 \times \mathbf{10^{19}}$.

---

[1] See H. Fletcher. *Le Radium*, **8**, 279, 1911.

MEAN KINETIC ENERGY OF A MOLECULE AT 0° C.

We have already seen that the mean kinetic energy of a molecule is given by the expression—

$$w = \frac{3}{2}\frac{RT}{N}.$$

Setting $R = 83{\cdot}2 \times 10^6$ c.g.s. units, and employing the above value for N, *viz.* $6{\cdot}062 \times 10^{23}$, we find that at $T = 273$, $w = 5{\cdot}62 \times 10^{-14}$ ergs, or since 1 calorie $= 4{\cdot}184 \times 10^7$ ergs, $w = 1{\cdot}31 \times 10^{-21}$ cals. Millikan (*loc. cit.*) gives $w = \mathbf{5{\cdot}621} \pm 0{\cdot}006 \times \mathbf{10^{-14}}$ ergs. This is the mean kinetic energy of a molecule at 0° C., and is independent of the physical state of the substance considered. It may be mentioned that this kinetic energy in the case of a gas or liquid represents energy of translation, in the case of a solid energy of vibration, for free translation is not possible in a solid.

Note.—As regards the question of the *type* of motion in solids see Vol. III.

THE MASS OF ONE MOLECULE OF HYDROGEN.

The value for the mass of the hydrogen molecule is obtained directly by dividing the molar weight, 2, by $N = 6{\cdot}062 \times 10^{23}$. The result is $3{\cdot}3 \times 10^{-24}$ gram, whence the mass of the hydrogen atom is $1{\cdot}65 \times 10^{-24}$ gram. Millikan (*loc. cit.*) gives as the most accurate value for the mass of the hydrogen atom $\mathbf{1{\cdot}662} \pm 0{\cdot}002 \times \mathbf{10^{-24}}$ gram.

THE MASS OF THE ELECTRON.

We have already seen that the mass of one hydrogen atom is 1830 times that of an electron or corpuscle. It follows therefore that the mass of an electron is $9{\cdot}0 \times 10^{-28}$ gram. Strictly speaking this value is only correct for an electron which is either at rest or moving with a velocity small compared with the velocity of light. If the electron is travelling with a velocity comparable with that of light its mass increases. Thus when its velocity is 90 per cent. of that of light the apparent mass is 1·81 times the value quoted. Theoretically when the electron attains the velocity of light its mass is infinite. Naturally this stage is never reached under any experimental conditions. The cause of this alteration in mass is due to the fact that the mass of an electron is electromagnetic. This is very briefly referred to later.

THE RÔLE OF ELECTRONS IN METALS.

Metals are noted for the property which they possess of conducting electricity and heat. Since the introduction of the concept of the electron considerable advance has been made in our knowledge of the solid state from this standpoint. Unfortunately there is no space in a book of this nature to consider this problem further. Mention can only be made of one very important relation which the electron theory as applied to metals (after certain simplifications have been introduced) predicts, namely, that the ratio of the thermal conductivity to the electrical conductivity should be a *constant* independent of the nature of the metal, and depending directly upon the absolute temperature. This relation, which was known as a purely empirical one under the title of the Wiedemann-Franz Law, possesses very considerable experimental support. For the method of deducing the relation referred to the reader must consult Sir J. J. Thomson's books already mentioned, and especially the papers of O. W. Richardson, to whom we are indebted for the greatest advances in this field (O. W. Richardson, "Electron Theory of Metallic Conduction," *Transactions of the Amer. Electrochem. Soc.*, **21**, 69, 1912, gives a good summary of the present position). It should be pointed out that rather remarkably the development of the unitary theory of radiant energy (see Vol. III.) in the hands of Nernst and Lindemann has led these authors to the conclusion that free electrons are *not* the main cause of thermal conduction. The evidence is therefore at the present time somewhat conflicting.

THE VARIOUS SOURCES OF CORPUSCLES OR ELECTRONS.

Cathode rays are not the only source of electrons. Mention has already been made that electrons are given out (along with other sorts of radiation) by radium and other radioactive materials during their decomposition. They are also given out, though to a much less extent, by other metals, such as the alkalies and alkaline earths, as well as by some amalgams, especially when these substances are heated or exposed to light—light, in fact, causes the expulsion of electrons from most metals, particularly if the light is of very short wave length (ultra-violet), such effects being known as "photo-electric effects". Electrons are also emitted when salts are vaporised in gas flames. The important thing is that whatsoever its source the ratio of $\frac{e}{m}$ for an electron is constant. It seems natural, therefore, as Sir J. J. Thomson says, "to regard it as one of the bricks of which atoms are built up".

Regarding the *origin* of the mass of an electron little can be said here beyond the fact that Sir J. J. Thomson has shown that its energy, and therefore its mass, is really due to energy of the ether—the medium which fills all space and transmits light and electromagnetic waves in general. But the whole question of what we mean by the "ether" has been rendered decidedly vague by the new work on radiation (*cf.* Vol. III.).

THE STRUCTURE OF THE ATOM.

Since an atom is electrically neutral, it is evident that it must contain a quantity of positive electricity equivalent to the sum of the charges on the electrons. We know very little indeed about the positive electricity, and the simplest assumption to make, therefore, is that it occurs as a sphere of uniform density throughout which the electrons are distributed.[1] This sphere attracts the corpuscles to its centre, their mutual repulsions tending to drive them away from one another, so that the "fabric" of the atom as a whole is in equilibrium when the repulsions just balance the attraction. The problem first studied by Sir J. J. Thomson is to find how electrons will distribute themselves in a sphere of positive electricity when successive additions are made to the number of electrons in the system. The problem soon becomes too difficult to treat mathematically if we consider the distribution in *three* dimensions in space. A simpler case is to consider the distribution in *one* plane (two dimensions) only—the plane being one which passes through the centre of the atom. The results obtained by Sir J. J. Thomson, though not complete, are sufficient to indicate in a general way the solution of the problem. If the system contains one electron it will evidently go to the centre of the sphere. If two electrons are present they will take up positions at two points A and B, situated along a straight line which passes through the centre O of the sphere, so that OA = OB = one-half the radius of the sphere. Three electrons will distribute themselves at the apices of an equilateral triangle, any side of which is equal to the radius of the sphere. Four electrons cannot be in equilibrium in one plane. If we consider for a moment the distribution in tridimensional space, the equilibrium arrangement is reached when the electrons are at the corners of a regular tetrahedron, whose centre is the centre of the sphere, and whose side is equal to the radius of the sphere. Returning to the case of distribution in one plane, we find that five electrons will be in equilibrium in a single ring formation, *i.e.* at the corners of a regular pentagon. Six electrons will, however, not be in equilibrium at the corners of a regular hexagon. Instead, one electron goes to the centre, and the remaining five form a regular pentagon. This is a "two-ring" system. Similarly eleven electrons distribute themselves, so that there are two forming the inner "ring" and nine in the outer. With successive additions one finds that the two-ring system becomes unstable, and a three-ring system makes its appearance. This happens when seventeen electrons are present, and the three-ring system persists until we reach thirty-two electrons, when a four-ring system appears. In this way we can go on adding electrons, thereby building up "atoms" of higher atomic weight. The above results (and others in which still greater numbers of electrons are considered) were obtained by mathematical analysis. They can also be demonstrated by a very ingenious experimental analogy, due originally to Mayer. For this purpose a number of small magnetised needles take the place of the corpuscles. The needles, which are all magnetised in the same way, are stuck through corks and floated upon water. The *rôle* of the sphere of positive electricity is taken by a large magnet suspended above the water, with its N pole pointing downwards if the S poles of the magnetised needles point upwards. On adding the needles one at a time various equilibrium configurations are obtained very similar to those already given. From one to five magnets, the single ring is stable; with six magnets one goes to the centre, the remaining five being equally distributed around it, and so on.

---

[1] Recent work of Rutherford and others (*Phil. Mag.*, 1913, 1914) points to the existence of a positive nucleus round which electrons rotate in various orbits. This is considered in Vol. III.

An important feature of the distribution of electrons is the recurrence of similar *types* at intervals. Thus the "atom" containing one electron has this electron at the centre. The "atom" containing six electrons has again one at the centre, the remainder forming the outer ring of the two-ring system, 1,—5. The "atom" with seventeen electrons is three-ring, one electron being in the centre, then a ring of five, and lastly a ring of eleven, thus, 1,—5,—11. The "atom" of thirty-two electrons is four-ring, one electron in the centre, then a ring of five, then a ring of eleven, and lastly a ring of fifteen, that is, 1,—5,—11,—15. Similarly, the "atom" which has forty-nine electrons in five rings is built up on the following type: 1,—5,—11,—15,—17. The "atoms" which consist of 1, 6, 17, 32, and 49 electrons have therefore a similar constitution. We would expect that physical and chemical properties which must depend ultimately upon atomic structure would likewise be similar in these cases. At the same time the "atoms" in which the number of electrons lies between six and seventeen, or between seventeen and thirty-two, or between thirty-two and forty-nine, are not built up on the 1,—5,—11,—15,—17 plan. The properties of these intermediate members would, therefore, differ from those previously considered. We thus see that the electron theory leads one to expect that there will be a *periodicity* in the properties of the atoms as the atomic weight increases. This is simply the Mendeleef-Meyer Periodic Law. It is clear that we have here strong evidence in favour of the electronic structure of atoms, since this theory predicts at least qualitatively the law which forms the most fundamental generalisation of systematic chemistry.[1]

As regards the *actual* number of electrons in atoms information is scanty. Attempts which have been made in this direction indicate, however, that the number is small, roughly of the order of one half of the relative atomic weight, *i.e.* the sodium atom contains eleven electrons. It is clear, therefore, since an electron possesses only $\frac{1}{1830}$ part of the mass of a hydrogen atom, that the main source of the mass of an atom must be due to the *positive* electricity contained in it. This brings us to the consideration of some very ingenious speculations regarding the *rôle* played by the positive electricity in the building up of atoms.

---

[1] As regards valency, which appears to be the lines of force produced by the transfer of an electron, the reader is referred to N. Friend's *Valency* in Sir W. Ramsay's series.

NICHOLSON'S THEORY OF THE STRUCTURE OF ATOMS. (*Phil. Mag.*, **22**, 864, 1911.)

The main difference between this theory and that of Sir J. J. Thomson lies in the question of the distribution of the positive charge. We have already seen that Sir J. J. Thomson considers the atom as consisting of a number of electrons dispersed throughout a sphere of positive electricity; this assumption being indeed made for the purpose of simplicity of treatment rather than as actually representing the physical facts. Nicholson's view is that the positive electricity exists in the atom like the electrons in *discrete portions*, each of uniform density; and further, these units are *small* in radius compared with the distance between the electrons themselves. At the same time, these "positives" are regarded as the source of nearly the whole mass of the atom. The atomic system is, therefore, planetary. "In a complex atom, built up of simpler systems, the assemblage of positive charges is in many respects similar to the assemblage of electrons which revolve round them, and it is not unlikely that many of the positive charges would also revolve. But they are not all of the same size, although the difference in size is not great. Their mass is so great that a disturbance which could expel one of them from an atom would also expel many of the attendant electrons, and it would be impossible to isolate a positive charge." This is in agreement with experiment up to the present (1914) as regards the isolation of the positive unit, although evidence of the existence of such is afforded indirectly.[1] Evidence in favour of Nicholson's theory is afforded by Sir William Ramsay's discovery that Radium Emanation or Niton—itself the newest member of the series of monoatomic gases—gives rise to the element Helium. "Unless the constituents of this atom already exist as a group in unstable equilibrium with other groups, in the atom of the emanation, it is difficult to imagine by what means it can be detached as such when a really definite conception of the process is intended." Evidently the difficulty is extreme on Sir J. J. Thomson's view of the atom, nor is it less on Rutherford's view that the atom is a simple Saturnian system involving only a single positive nucleus.

In building up the atoms of the elements Nicholson finds it necessary to postulate the existence of three protyles, namely, hydrogen, a hypothetical element which he calls "nebulium,"[2] and another hypothetical element which he calls "protofluorine". The hydrogen atom is assumed to possess three electrons, nebulium four, and protofluorine five. The element containing two electrons he identifies with coronium, an element in the sun's corona, but does not appear to require this in building up the other (known) elements.

As regards atomic weights, according to Nicholson we must accept the fact that all inertia (*i.e.* all *mass*) is due to electric charges in motion, which we have already mentioned as having been shown to be the case by Sir J. J. Thomson in connection with the mass of an electron.

---

[1] See R. W. Wood, *Phil. Mag.*, February, 1908.

[2] Nebulium is perhaps *not* hypothetical, see page 50.

The weight of an atom always determined from its inertia may be regarded as the sum of the inertias of all its positive and negative charges. If the positive charges have a much smaller radius their inertia will greatly overweigh that of the electrons, and we may neglect the latter for the present. The motions to which a positive nucleus is subject will always be slow compared with the velocity of light. Let r be the radius of the positive, and let e be the charge upon an electron. If there are n electrons in a neutral atom of a primary simple substance (containing only one nucleus) the positive charge is ne, and the inertia of the nucleus and, therefore, of the whole atom approximately is proportional to $\frac{n^2e^2}{r}$ by the usual formula[1] for slow motions. If the positive electricity has uniform volume density, its volume is proportional to ne, therefore its radius r is proportional to $(ne)^{\frac{1}{3}}$, or $n^{\frac{1}{3}}$, since e is a constant. *Thus the inertia or mass of the atom is proportional to* $n^{\frac{5}{3}}$ *from the above formula.* The mass of a compound atom containing several nuclei associated with rings of electrons will be proportional to $\Sigma n^{\frac{5}{3}}$. Assuming that the hydrogen atom has three electrons, the relative weights of the atoms of the primary substances are:—

Coronium	$n = 2$,	$n^{\frac{5}{3}} = 3·1748$
Hydrogen	$n = 3$,	$n^{\frac{5}{3}} = 6·2403$
Nebulium	$n = 4$,	$n^{\frac{5}{3}} = 10·079$
Protofluorine	$n = 5$	$n^{\frac{5}{3}} = 14·620$

Taking the atomic weight of hydrogen to be 1·008, the above substances have the following relative atomic weights:—

---

[1] An uncharged body of mechanical mass m, travelling with velocity v, possesses kinetic energy $\frac{1}{2}mv^2$. If the body is electrically charged, it sets up a magnetic field round it in virtue of its motion, and this field contains energy given by the expression $\frac{1}{3} \cdot \frac{e^2v^2}{r}$, where e is the charge and r the radius of the body. The energy which has to be supplied to keep the charged sphere in motion is $\frac{1}{2}mv^2 + \frac{1}{3} \cdot \frac{e^2v^2}{r}$ or $\frac{1}{2}\left(m + \frac{2}{3}\ \frac{e^2}{r}\right)v^2$. The body acts, therefore, as if it possessed the mass $\left(m + \frac{2}{3} \cdot \frac{e^2}{r}\right)$. A rough analogy is afforded by the motion of a particle through a viscous fluid, for, as the particle moves, it carries some of the fluid along with it, thereby apparently increasing its own mass. If r were one or two centimetres, the term $\frac{2}{3} \cdot \frac{e^2}{r}$ would be quite negligible compared with the mechanical mass m. If r is of the order of the diameter of an electron, Sir J. J. Thomson has shown that m is negligible compared to $\frac{2}{3} \cdot \frac{e^2}{r}$. Hence the same conclusion is justifiable in connection with the small positive nuclei of Nicholson. For this reason the mass or inertia is placed proportional to the term $\frac{n^2e^2}{r}$.

Coronium	0·51282	
Hydrogen	1·008	(Oxygen = 16)
Nebulium	1·6281	
Protofluorine	2·3615	

We can now consider compound atoms built up out of these primaries. Nicholson, as already mentioned, did not find coronium necessary apparently for this purpose; a fact which is somewhat surprising. Neglecting the mass of the electrons in comparison with the mass due to the positive nuclei (although n in the expression $n^{\frac{5}{3}}$ is actually the number of electrons), Nicholson suggests that the helium atom is made up of one atom of nebulium (Nu), and one atom of protofluorine (Pf). Writing this in the form of a chemical equation—

$$1\text{He} = 1\text{Nu} + 1\text{Pf or NuPf}$$

Atomic weight of Nu = 1·6281
Atomic weight of Pf = 2·3615

Sum = 3·9896, At. weight of He = 3·99.

According to Nicholson, "there is a fairly general suspicion that many of the elements may be composed of helium and hydrogen". Thus boron (atomic weight 11) might be 2He + 3H. When the helium "group" (on the above hypothesis) enters into the composition of another more complex atom it is not implied that this group actually exists as in free helium atoms, but its two component groups Nu and Pf may be present, though occupying different relative positions from those which they occupy in the helium atom. A few typical instances of Nicholson's method of building up compound atoms may be given.

Argon.—The atomic weight is 39·88. 10He = 39·9.

Carbon.—The atomic weight is 12·00. The combination (2He + 4H) gives the atomic weight 12·008.

Oxygen.—The atomic weight is 16·00. The combination (3He + 4H) gives 15·996.

Fluorine.—The atomic weight is 19·0. The combination (3He + 7H) gives 19·020.

Neon.—The atomic weight is 20·21. The combination (6Pf + 6H) gives 20·21.

"Apparently the group (3Pf + 3H) or $(\text{PfH})_3$ has considerable significance in atomic structure, according to the present theory."

For further applications of this theory the reader must consult the original paper. It must, of course, be pointed out that at the present stage these considerations are of a speculative nature. Nicholson's speculations are of particular interest in view of the recent experiments of Collie and Patterson, to which reference will be made shortly. The real importance of Nicholson's views lies in the fact that a definite *rôle* is assigned to the positive charge resident in the atom, and, at the same time, the number of electrons (n) enters in a logical manner into the term for the atomic weight, although this "weight" is essentially due to the positive nuclei. It should be noted that the most crucial test of the above views is to be found in the calculation of the atomic weights of elements which possess small atomic weights, such as helium, lithium, beryllium, etc.; in the case of elements with higher atomic weight, which might possibly be built up out of more than one combination of the protyles, the assigned structure is of less importance. In Vol. III. an account is given of another theory of the atom due to Bohr which has much in common with the theory of Nicholson.

H. W. Nicholson (*Proc. Roy. Astron. Soc.*, **72**, 49, 1911) has calculated the chief spectral lines of the hypothetical element nebulium, which, according to his theory, contains four electrons rotating round a positive nucleus whose charge is $4e$. This arrangement represents a neutral atom. If one electron is missing, the other three can take up equidistant positions and rotate in a new orbit, the system consisting now of one atom of nebulium with a single positive charge in excess (the nucleus being still $4e$). Also the atom may acquire a negative charge by taking up one or more electrons. The neutral, positive, and negative atoms respectively give rise to different lines in the spectrum. Nicholson found that the spectrum lines of certain nebulæ—principally the Orion nebulæ—which have hitherto been assigned to an unknown element or elements could, with the exception of two lines, be accounted for quantitatively by the vibrations of the atomic system charged and uncharged, which he has called nebulium. This result affords a certain amount of evidence in favour of Nicholson's theory of the structure of atoms.

THE DISINTEGRATION OF THE ATOM. RADIOACTIVITY.

We are already familiar with the existence of small electrically charged particles as being the principal constituents of all atoms. Further, we have seen that negatively charged particles—the electrons—may be obtained from a variety of sources. A source of special interest is the group of chemical substances known as the radioactive elements. The typical radioactive metals are: uranium, actinium, radium, and thorium. Radioactive substances, as the name implies, are characterised by the property of emitting radiations which can be detected by the electrical or photographic effects produced by them. These radiations have been divided into three classes—α rays, β rays, γ rays.[1]

The α rays are positively charged particles shot off from the radioactive substance with considerable velocity. They can, with difficulty, be deviated by a strong magnetic field, and the direction of deviation indicates the sign of their charge. Their mass is comparable with that of the helium atom—four times that of the hydrogen atom, and each carries two positive charges ($2e$). In their passage through a gas they cause ionisation of the gas,[2] which thereby becomes a conductor of electricity. This ionising power depends upon the velocity of the particles, a good ionising agent such as the α particles not possessing extremely great velocity, and therefore not possessing a very great penetrating power. Thus, by enclosing the radioactive substance in a glass tube, the α radiations are completely stopped by sufficiently thick walls.

---

[1] A further variety, known as Δ rays, has also been investigated.

[2] For an account of the mechanism of the ionisation process the reader should consult Townsend's book on *Ionization of Gases by Collision*.

Besides α particles, some radioactive substances emit negatively charged particles called β rays, which are identical with cathode rays or electrons. The velocity with which they are emitted varies greatly from case to case. These rays are deviated easily by a magnetic field, and in the opposite sense to that experienced by the α rays. Their mass is only $\frac{1}{1800}$ part of one hydrogen atom. They possess much greater penetrating power than α rays, and therefore in their passage through a gas produce much *less* ionisation. These β rays escape, at least in large proportion, through the glass walls of the tube enclosing the radioactive substance.

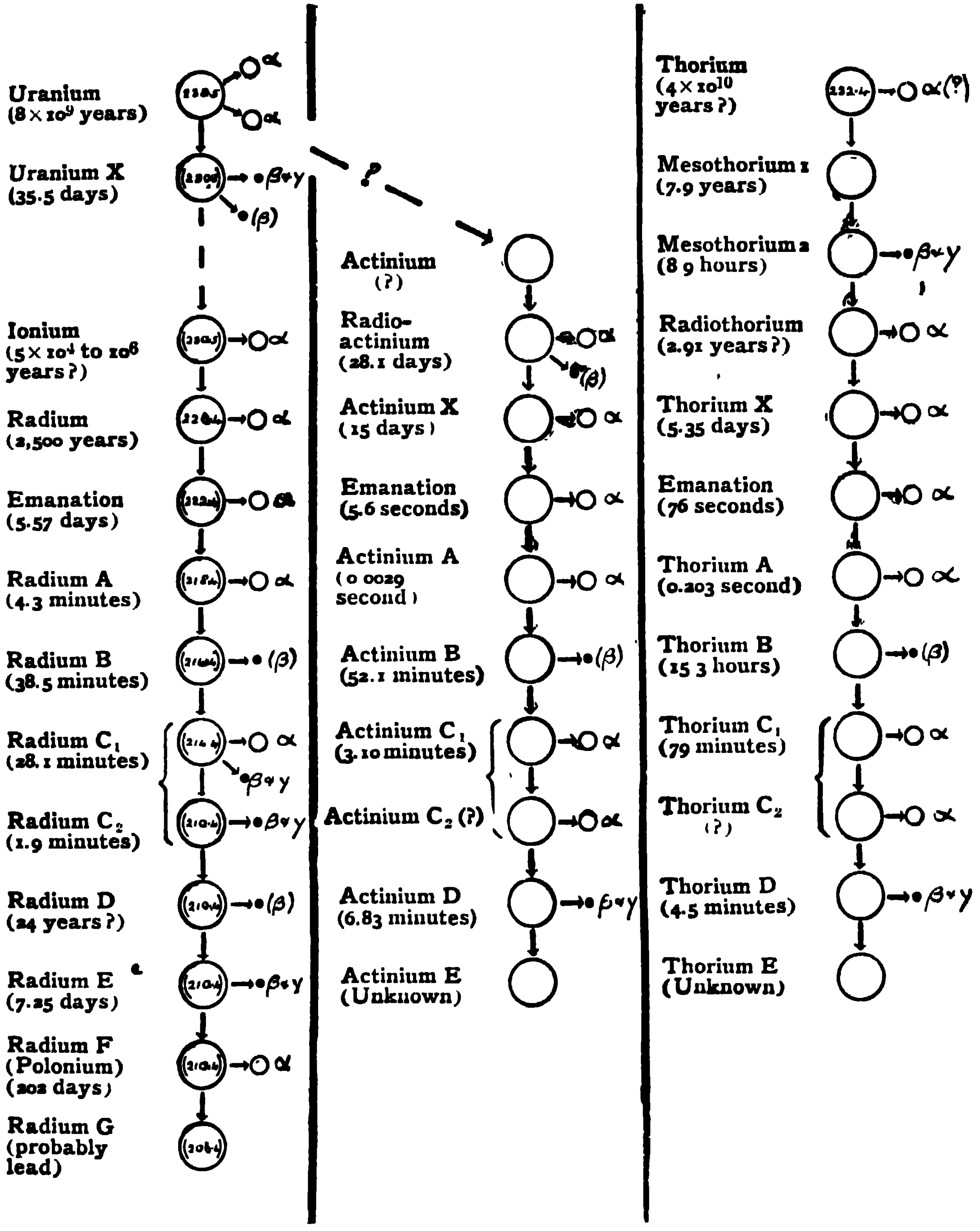
In addition to the *material* radiations (α and β rays) some radioactive substances can also give rise to a third kind of radiation called γ rays, which are characterised by the property of being non-deviable by a magnetic field. At the present time there are conflicting views regarding the actual "constitution" of these rays. At any rate, they are not a stream of material particles as the α and β rays are. One view is that they consist of ether pulsations analogous to Röntgen rays. γ rays are the most penetrating type of radiation, and are therefore least effective in producing ionisation in a gas.

A large number of successive radioactive transformations have been observed up to the present time. At each transformation one practically always finds one or other of the above types of rays given out, the γ ray generally accompanying the expulsion of a β particle. In the accompanying table is given the chronology of these transformations as far as they are known at present. Each substance is identified not by "chemical" properties, the quantity present being exceedingly small, but by the duration of its radioactivity. A single isolated radioactive body will gradually lose its activity, the law of radioactive decay being the simple exponential one—

$$I = I_0 e^{-\lambda t}$$

where I_0 is the initial activity of the body, I the activity at a time t, and λ a constant which characterises the substance in question. The activity is measured by the rate at which a gold-leaf electroscope is discharged. From the observed rate of decay one can calculate λ, and from this one can easily find the time required for a given radioactive body to lose one-half of its radioactivity. This time is called the "half-life" period.

The table is taken by permission from F. Soddy's monograph on *The Chemistry of the Radio Elements*, in Findlay's series. The time periods given in connection with each substance represent the "periods of average life," which are 1·45 times the half-life period. The nature of the rays emitted by each product is also indicated.



There are a number of gaps in the above table, indicating that there are other products which have as yet remained undiscovered. Further, it is now recognised that side-chain products have to be anticipated; that is, the production of two or more substances apparently simultaneously from one parent substance. The theory which was first advanced by Rutherford to account for the existence of radioactivity and the relations of radioactive substances to one another, is that the radioactive atom disintegrates or breaks down, emitting a ray of some kind, and leaving a residue of smaller atomic weight which possesses properties differing from the parent substance. This residue in its turn may disintegrate in a similar manner. It is evident that the expulsion of an α particle causes a much greater decrease in the atomic weight of the residue than the expulsion of a β ray, since the mass of an α particle is approximately six thousand times as great as that of an electron. An adequate account of radioactivity in general cannot be given within the compass of a few pages. A few typical examples of the rate of radioactive change will be taken up later as illustrations of chemical kinetics; but for further details the reader must consult Rutherford's book on *Radioactivity*, or Soddy's *Interpretation of Radium*, and *The Chemistry of the Radio Elements*, or Makower's *Radioactive Substances*.

As regards the significance of the phenomenon of radioactivity from the standpoint of the structure of the atoms of the elements the most interesting fact is the observation made by Ramsay and Soddy in 1903, that radium emanation (which is a gas, and has been shown recently by Ramsay and Gray to belong to the rare gas group under the name niton) obtained from radium bromide gradually developed *the helium spectrum*, giving the characteristic yellow line. This is the first instance of the transmutation of the elements, and it shows that the electrical grouping constituting the helium atom must have been present originally in the heavier radium atom. It is now known with considerable certainty that the helium atom is simply an α particle which has lost its (double) positive charge. Helium can therefore be formed at all those stages at which α particles are emitted. Such evidence as this is, of course, strongly in favour of an electrical corpuscular constitution of all atoms, and this is borne out by the fact that radioactivity is not confined to a few metals, but is—although to a much smaller degree—a general property of ordinary metals as well. In the same connection, and especially with regard to Nicholson's theory of the structure of the atom, the recent discovery of Collie and Patterson (*Journ. Chem. Soc.*, **103**, 419, 1913) of "the presence of neon in hydrogen after the passage of an electric discharge through the latter at low pressures" is of the utmost importance. In this work all conceivable precautions were taken to avoid any leakage of air into the apparatus. One of the final forms of the apparatus consisted of a double-walled glass tube, the discharge being passed through the *inner* tube which contained hydrogen, the outer tube being at a high vacuum. After continuous sparking for some hours it was discovered that quite appreciable quantities of helium and neon were present in the *outer* tube, and likewise a smaller amount of neon in the *inner*. During the progress of the sparking the greater bulk of the hydrogen itself had disappeared. Although the authors are careful to avoid the expression of any views regarding the mechanism of the production of these gases, the experimental fact remains as an extremely suggestive one from the standpoint of atomic structure and transmutability of so-called "elementary" atoms.

CHAPTER II.

Distribution of molecules in space—Physical equilibrium—The continuity of the liquid and gaseous states, from the kinetic standpoint—The solid (crystalline) state—Distribution of atoms in space in crystals.

HAVING considered the actual existence of molecules, it is necessary to go a little more closely into the question of how these distribute themselves in space under given conditions of temperature and pressure. Although the subject will be treated in the present instance from the standpoint of purely "physical" equilibrium, it must not be forgotten that "chemical" effects, such as polymerisation of molecules on the one hand, or dissociation on the other, enter in certain cases: and indeed when we find that the system under consideration exhibits divergencies in behaviour from what might be expected upon purely physical or mechanical grounds, we are practically forced to conclude that the discrepancies are due to more strictly "chemical" change. It is, however, of extreme importance to treat the problem—at least as far as we are able—from the standpoint of molecular mechanics, as has been done to a large extent for gases and liquids in the so-called "theory of the continuity of state".

The word "state" refers to a somewhat arbitrary division of matter in relation to a particular kind of molecular aggregation and orientation under given conditions of temperature and pressure, such molecular arrangements and relations being characterised by the presence or absence of certain physical properties. Each "state" represents the *equilibrium* distribution of the molecules forming the system. The fact, that at one and the same temperature two such different types of equilibrium distribution, as that represented by a liquid and its saturated vapour, exist, is sufficient to indicate that the attractive and repulsive forces operating between molecules are by no means simple, and indeed very little is known about it. We recognise three states of matter—solid, liquid, and gaseous. With the general characteristics of these states the reader is assumed to be familiar.

THE BEHAVIOUR OF GASEOUS SYSTEMS.

We have already seen in the introductory chapter that the law of Boyle (1662) and the law of Charles or Gay-Lussac (1808) may be combined in the equation—

$$\frac{pv}{T} \quad \text{constant.}$$

The numerical value of the constant depends obviously upon the units employed and the mass of gas considered. The molecular weight of a gas in grams we shall call the gram-molecule. The gram-molecule is the same multiple of the actual weight of a molecule, or the gram-molecule contains the same number of actual molecules for all substances whose molecules are normal, that is molecules neither polymerised nor dissociated. If we take the gram-molecule as our unit of mass and restrict our consideration to *gases* whose molecules are normal, we know by the hypothesis of Avogadro that the gram-molecule of any gas at a given temperature and pressure must occupy one and the same volume. Taking the gram-molecule as the unit of mass, it is usual to denote the constant in the above expression by R; that is

$$\frac{pv}{T} \quad R \text{ or } pv = RT.$$

It has been found that 1 gram-molecule of a gas at 273° absolute, and at 1 atmosphere pressure occupies a volume of 22·412 liters. Hence the value of

$$R \,.\, \frac{pv}{T} = \frac{22\cdot412 \times 1}{273} \; \frac{\text{liter atmosphere}}{\text{degree}}$$

or since 1 atmosphere = 10^6 dynes per square cm. approx., it follows that

$$1 \text{ liter atmosphere} = 1000 \times 10^6 \, \frac{\text{dynes} \times \text{c.cs.}}{\text{cm}^2.}$$

$$= 10^9 \text{ ergs.}$$

Further $\quad 1 \text{ calorie} = 4\cdot2 \text{ joules} = 4\cdot2 \times 10^7 \text{ ergs,}$

so that employing the calorie instead of the liter atmosphere as the unit of energy, we obtain for R the value of 1·98 approx.

The expression $pv = RT$ is known as "the gas law," and is taken as the criterion—or rather part of the criteria[1]—of a *perfect gas*. All actual gases approximate more or less closely to this ideal state, but none obey the gas law absolutely. We shall consider the behaviour of a few actual gases in some detail.

If Boyle's Law held rigidly for actual gases, then at constant temperature the product pv ought to be constant whatsoever the value of p. That pv is not quite independent of p, even for gases such as hydrogen, nitrogen, oxygen, etc., is evident from the following data obtained by Amagat (*Annales de Chim. et de Phys.* [6], **29**, 68, 1893). For gaseous substances such as ethylene and carbon dioxide, which at ordinary temperatures are much nearer their "critical point" than the gases above mentioned, the value of pv varies very much with change in p.

Values of pv *for hydrogen and nitrogen.*—[Note: The product pv is *arbitrarily* taken as unity under one atmosphere and at 0° C.]

---

[1] The remaining criterion of a perfect gas is that Joule's Law shall be obeyed, *i.e.* that the total energy shall be independent of the volume (*cf.* Vol. II., Chap. III.).

Hydrogen.			Nitrogen.		
p in Atmospheres.	$t = 0°$ C. (pv).	$t = 99·25°$ (pv).	p in Atmospheres.	$t = 0°$ C. (pv).	$t = 199·5°$ C. (pv).
1	1·0000	—	1	1·0000	—
100	1·0690	—	100	0·9910	—
150	1·1030	1·4770	150	1·0085	1·8620
200	1·1380	1·5135	200	1·0390	1·9065
400	1·2830	1·6590	400	1·2570	2·1325
600	1·4315	1·8040	600	1·5260	2·3840
800	1·5775	1·9490	800	1·7980	2·6400
1000	1·7200	2·0930	1000	2·0685	—

The following data refer to ethylene and carbon dioxide. The unit value is arbitrarily assigned to the product pv when p is 1 atmosphere and the temperature is 0° C. The values at this temperature are not reproduced owing to the fact that this being below the "critical temperature" liquefaction takes place at the higher pressures, the system becoming heterogeneous (liquid + vapour) thereby giving a discontinuous curve.

Ethylene (Gaseous).			Carbon Dioxide (Gaseous).		
p in Atmospheres.	10° C. (pv).	100° C. (pv).	p in Atmospheres.	50° C. (pv).	100° C. (pv).
1	—	—	1	—	—
50	0·4200	1·1920	50	0·9200	1·2065
100	0·3305	1·0050	100	0·4910	1·0300
150	0·4590	0·9240	125	0·3950	0·9470
200	0·5850	0·9460	150	0·4190	0·8780
300	0·8270	1·1330	200	0·5000	0·8145
400	1·0585	1·3560	400	0·8515	1·0385
1000	2·3205	2·6425	600	1·1865	1·3655
			1000	1·8140	1·9990

If ethylene obeyed the gas law $pv = RT$ rigidly, the value of pv on the above scale at 10° C. would have been 1·0366, at 100°, 1·3663. Similarly, the pv for carbon dioxide would have been 1·1832 and 1·3663 at 50° and 100° respectively. The behaviour of the four substances, hydrogen, nitrogen, ethylene, and carbon dioxide with respect to Boyle's Law is shown graphically on the accompanying diagrams (Figs. 10, 11, 12, and 13).

It will be observed that in no case is a horizontal line obtained such as Boyle's Law requires. Hydrogen alone throughout the temperature range given shows a steady rise in the value of pv as p increases; the other gases show first a decrease in pv to a minimum value followed by a rise for still higher values of p. The divergencies from Boyle's Law are due to two causes, (1) the volume of the molecules themselves, though small compared with the total space occupied by the gas, is not zero, and in many cases is by no means negligible; (2) there are forces of attraction sometimes of considerable magnitude operating between the molecules. These two effects in general oppose one another, and which will predominate depends on the conditions (T and p) of the system. The two effects referred to are taken account of, as we shall see, by terms involving two constants a and b in van der Waals' equation of state. The increase in pv with increasing p simply means that the gas is not compressible enough, *i.e.* v does not decrease as much as it would if the gas were perfect. The molecules themselves can only be regarded as very slightly compressible compared with the actual system,

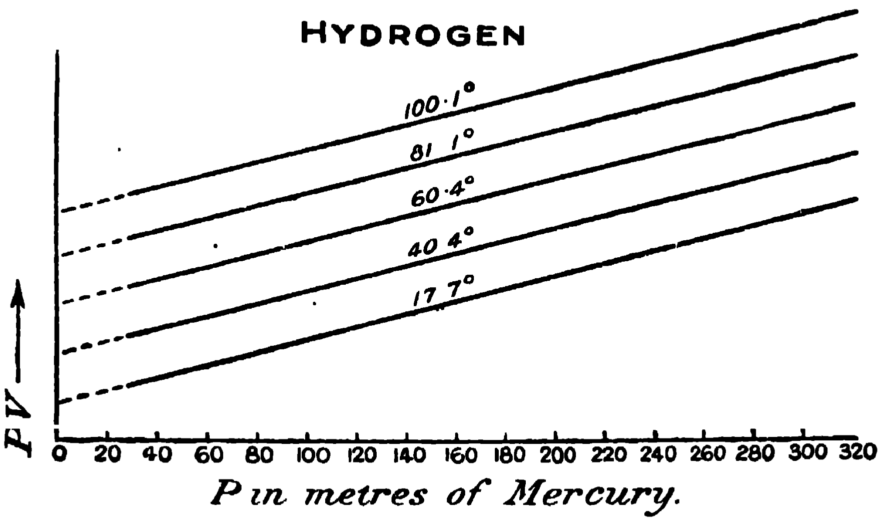


FIG. 10.

(E. H. Amagat, *Ann. Chim. et de Physique* [5], **22**, 370, 1881.)

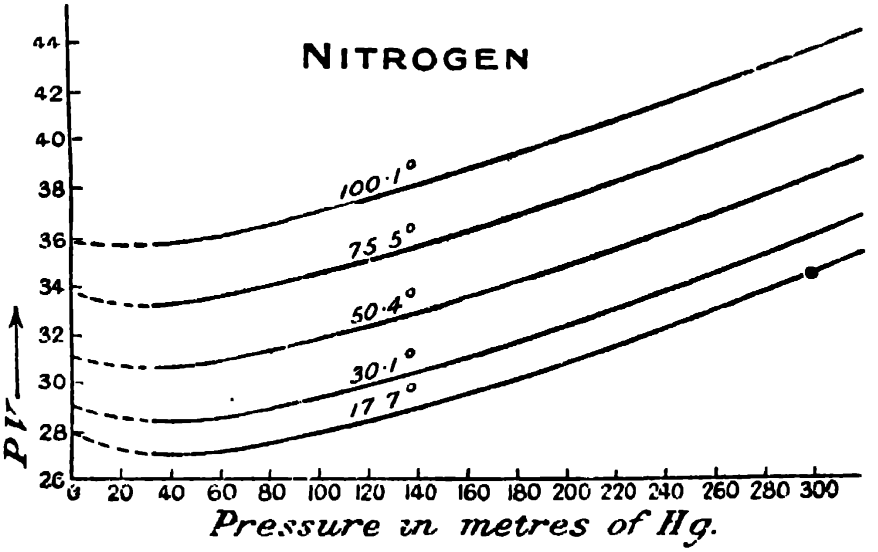


FIG. 11.

(E. H. Amagat, *ibid.*)

gas or liquid, in which the molecules are present. In fact, if we were able to compress a portion of matter sufficiently until the molecules came into contact with one another, any further increase of pressure would only have an infinitesimal effect upon the volume, and the product pv would *rapidly* increase with increase in p. The other effect mentioned, namely, the attraction between the molecules, has the opposite effect, that of making the gas too compressible (compared with the perfect gas) by drawing the molecules together. Owing to this attraction, the value of pv should diminish with increase in p. This is seen to be the initial resultant effect in ordinary gases (with the exception of hydrogen) up to certain pressure values, when the molecular-volume correction term predominates and the pv values begin to rise. This type of curve, in which a minimum is exhibited, may also be realised in the case of hydrogen, provided we work at a temperature considerably lower than that for which the data were quoted. This is considered in a more quantitative manner later.

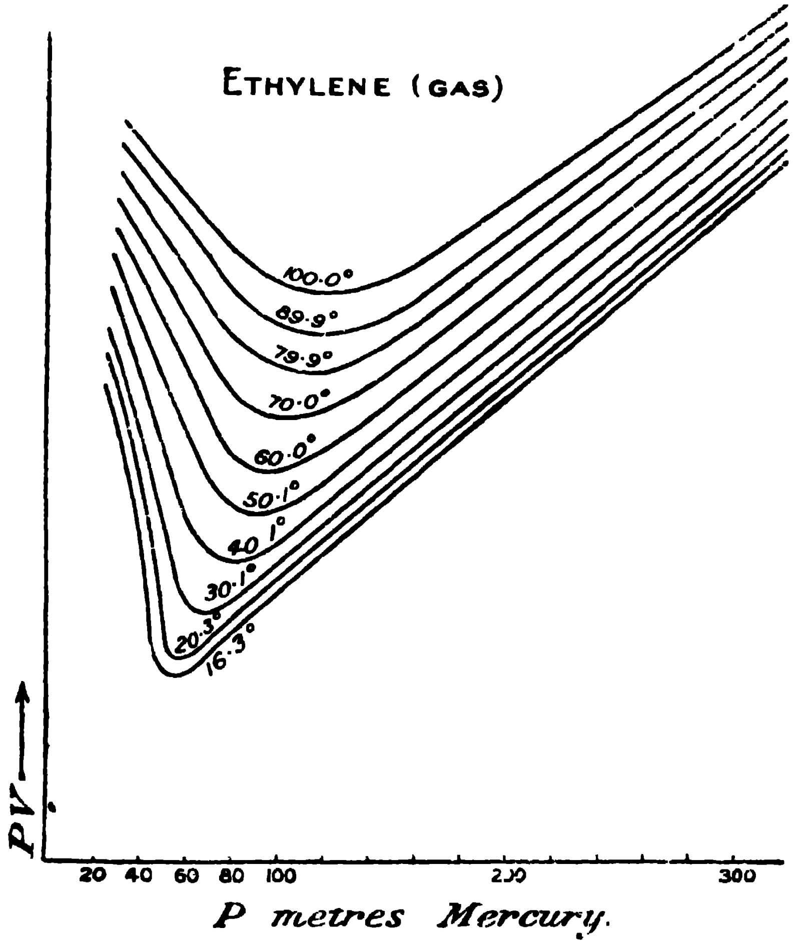


FIG. 12.

(E. H. Amagat, *Ann. Chim. et de Physique* [5], 370, 1881).

BEHAVIOUR OF SYSTEMS CONSISTING OF GAS AND LIQUID.

So far we have only considered systems which are entirely gaseous. It is well known, however, that under certain conditions a highly compressed gas may become partially liquid, condensation going on *without* increase of pressure but with great decrease of volume until the system becomes homogeneous once more, being now entirely liquid. The principle known as the *continuity of state* was first enunciated by Andrews to apply to such phenomena. According to Andrews, there is no essential difference between states of matter, the liquid and gaseous states being simply widely separated stages in a continuous series of changes. Andrews was the first to investigate the conditions under which a gas could or could not be liquefied. In this way he introduced the concept of *the critical state* involving *critical temperature*, *critical pressure*, and *critical volume*. Andrews found experimentally in the case of gases such as carbon dioxide, nitrous oxide, ammonia, and ether vapour, that there existed a certain temperature—the critical temperature—above which it was impossible to liquefy the gas, no matter how great the pressure. The minimum pressure which was just sufficient to cause the gas to liquefy at the critical temperature was

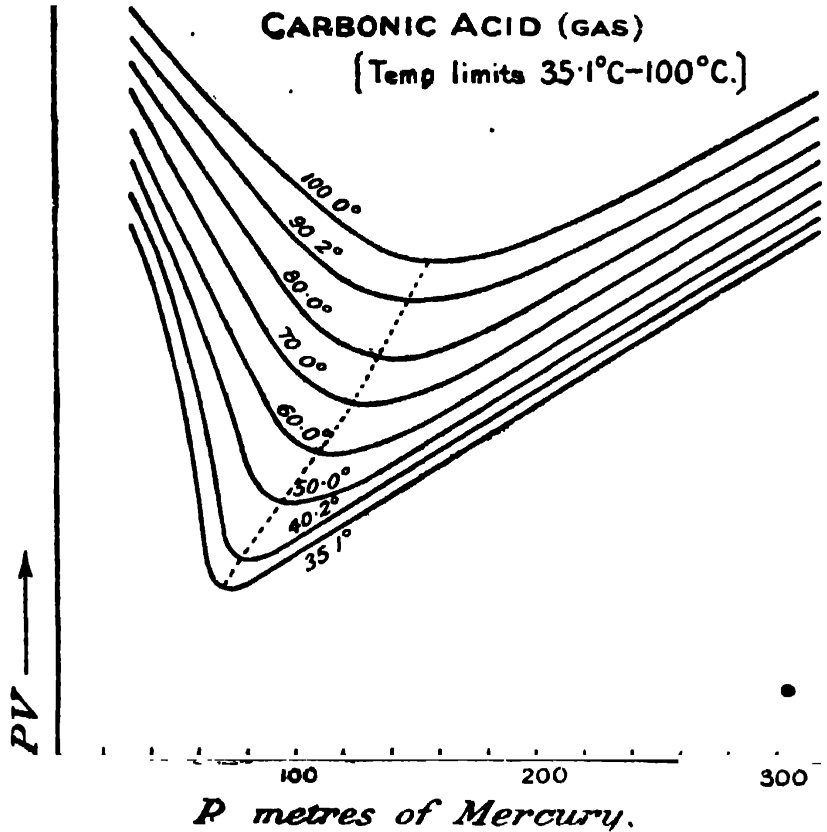


FIG. 13.

(E. H. Amagat, *Ann. Chim. et de Physique* [5], **22** 370, 1881.)

called the critical pressure, and the volume of unit mass of the gas at the critical temperature and pressure was called the critical volume. The following table (taken partly from S. Young's *Stoichiometry*,[1] partly from P. Walden, *Zeitsch. physik. Chem.*, vol. **66**, 1909, and partly from G. Rudorff, *Annalen der Physik* [4], vol. **29**, 1909) gives the values of the critical temperature in degrees centigrade, the critical pressure in atmospheres, and the critical density, that is the reciprocal of the critical volume, for a few substances:—

Substance.	Critical Temperature, ° C. t_c.	Critical Pressure, p_c (Atmos.).	Critical Density $= \frac{1}{v_c}$
Helium . . .	– 268	2·26	0·066
Neon . . .	lower than – 218	—	—
Argon . . .	– 117·4 (– 122·44)	50·6	0·509
Krypton . .	– 62·5	54·2	0·775
Xenon[2] . . .	+ 16·6	58·2	1·155
Hydrogen . .	– 238	13·4 to 15	0·043
Nitrogen . .	– 146	35	0·299
Oxygen . . .	– 119	50·8	0·4 to 0·65
Ethylene . .	+ 10·1	51·0	0·22 to 0·36
Carbon dioxide .	31·5	72·9	0·464
Ammonia . .	130	115·6	0·239
Ether . . .	193·8	35·6	0·2625
Carbon tetrachloride	283·15	44·97	0·5576
Isopentane . .	187·8	32·92	0·2343
Benzene . .	288·5	47·89	0·3045
Ethyl acetate . .	250·1	38·0	0·3077
Ethyl alcohol .	243·1	63·0	0·2755
Water . . .	360	195·5	0·2078
Hydrochloric acid .	52	86 to 96	0·61 to 0·462

A brief account of the methods whereby p_c, v_c, and t_c may be obtained will be given later.

It will be evident from the foregoing discussion that the simple gas law does not hold for actual gases or vapours. In the case of liquids the law breaks down entirely. In view of the close connection between the liquid and gaseous states other expressions have been proposed as possessing a more general applicability, these being called "characteristic equations," or "equations of state". Before considering some of these, however, it is convenient to consider still further some of the experimental data upon pressure, volume, and temperature in the case of carbon dioxide and isopentane, both liquid and gaseous.

---

[1] Young has recently published the recalculated data upon the vapour pressures, specific volumes, heats of vaporisation and critical constants of thirty pure substances (mainly organic) (*Proc. Roy. Dub. Soc.*, **12** [N.S.], 374-443, 1910).

[2] Patterson, Cripps, and Whytlaw-Gray, *Proc. Roy. Soc.*, **86** A, 579, 1912.

AMAGAT'S DATA (*l.c.*) ON THE VARIATION OF *pv* WITH *p* FOR CARBON DIOXIDE AT TEMPERATURES BELOW THE CRITICAL POINT.

p in Atmospheres.	*pv* at 0° C.	*pv* at 30° C.
1	1·0000 (arbitrary unit)	—
50	0·1050	0·7750
100	0·2020	0·-550
200	0·3850	0·4400
400	0·7280	0·7950
600	1·0495	1·1275
1000	1·6560	1·7480

At low pressures the system is entirely gaseous, at higher pressures it becomes liquid. The product *pv* is not even approximately constant. The accompanying diagram (Fig. 14) illustrates the relation of *pv* to *p* over the temperature range 0°-258° C.

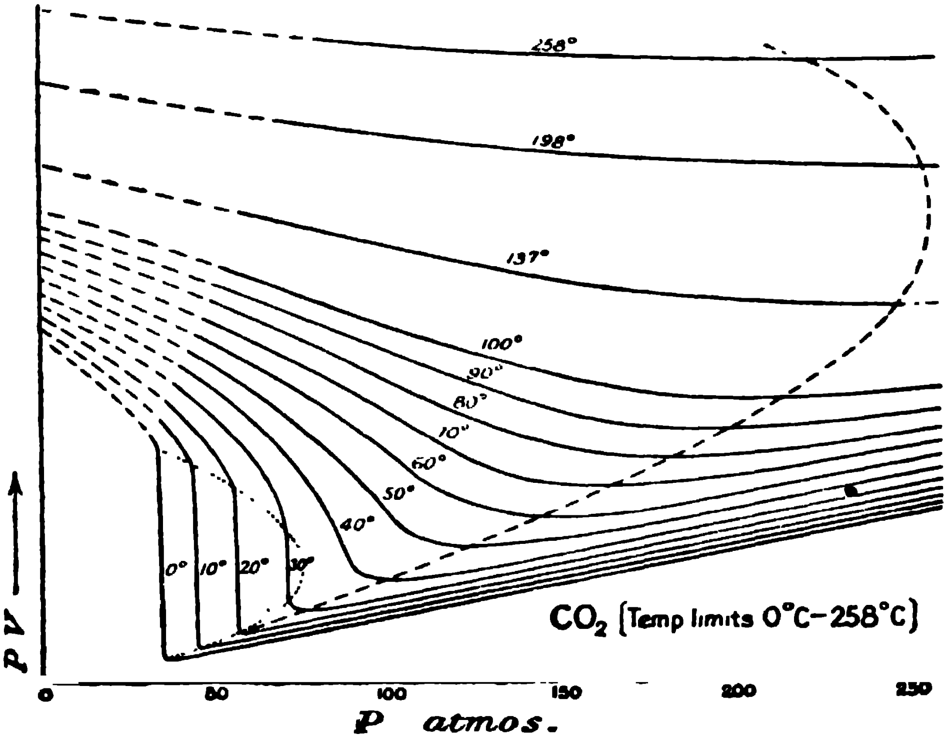
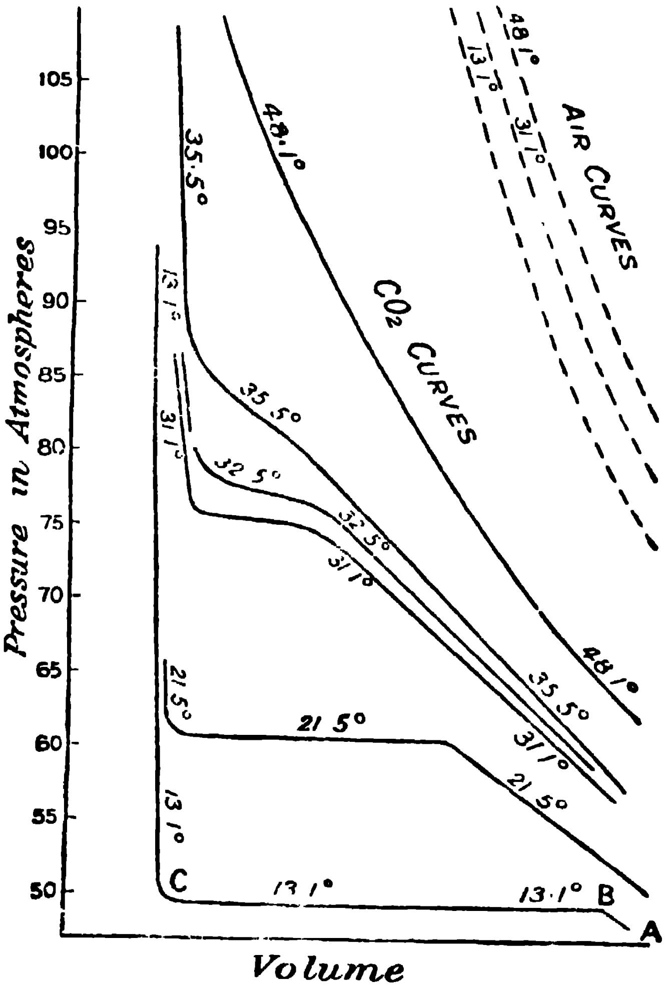


FIG. 14.

If CO_2 were a perfect gas the diagram would consist of a series of horizontal lines.

Let us now look at the behaviour of the same substance from a slightly different standpoint, namely, the variation of *v* itself with *p* at a series of different temperatures. This was first done by Andrews, and his curves are reproduced in Fig. 15. Each line represents the relation between *p* and *v* at a given temperature, such lines being known as the isothermals of the system. The same *mass* of carbon dioxide is employed throughout. Consider the isothermal corresponding to the temperature 13·1° C. At low pressures the volume (A) is large. As the pressure is increased the volume decreases nearly proportionally, *i.e.* Boyle's Law is very nearly obeyed. When a certain volume (B) is reached partial liquefaction takes place and the pressure of the system remains constant while the volume diminishes, the isothermal being horizontal. This state of things holds good until the system has so decreased in volume that it becomes entirely liquid at (C). To cause any further decrease in v a large increase of pressure is required, so



ANDREWS' CO₂ CURVE

FIG. 15.

that the isothermal becomes nearly vertical. At the temperatures 21·5° C. and 31·1° C. the same kind of behaviour is observed except that at the higher temperatures the horizontal portion of the isothermal (that part which corresponds to the simultaneous existence of liquid and vapour) becomes rapidly shorter, and, in fact, at 32·5° there is no horizontal portion at all, *i.e.* the system does not liquefy. The critical temperature of CO_2 lies between 31·1° and 32·5°. At higher temperatures, therefore, the system is homogeneous and gaseous, no matter what pressure may be employed to compress the gas. The higher the temperature the more nearly do the isothermals approximate (compare the isothermal at 48·1°) to those which would be given by a perfect gas (rectangular hyperbolæ). For the sake of comparison, Andrews includes the curves for air. At ordinary temperatures air approximates fairly closely to the behaviour of a perfect gas, since the critical temperatures of nitrogen and oxygen lie very much below room temperature.

To return to the case in which liquid and gas (*i.e.* saturated vapour) are in contact, the gradual change in the density of each phase with temperature and the approximation of the phases to identity which is realised at the critical point are apparent from the following results obtained by Amagat (*l.c.* 1893) in the case of carbon dioxide:—

t° Centigrade.	Density of Liquid.	Density of Saturated Vapour.	Pressure Exerted by System.
0	0·914	0·096	34·3 atmos.
5	0·888	0·114	39·0 „
10	0·856	0·133	44·2 „
15	0·814	0·158	50·0 „
20	0·766	0·190	56·3 „
25	0·703	0·240	63·3 „
28	0·653	0·282	67·7 „
29	0·630	0·303	69·2 „
30	0·598	0·334	70·7 „
30·5	0·574	0·356	71·5 „
31	0·536	0·392	72·3 „
31·25	0·497	0·422	72·8 „
31·35	0·464	0·464	72·9 „

Hence critical temperature = 31·35° C.; critical pressure = 72·9 atmospheres; critical volume = $\frac{1}{0·464}$ c.c.

If the values of the densities of liquid and vapour are plotted against temperature, one obtains a closed curve of the shape shown in Fig. 16.

If the *mean* value of the density of liquid and density of vapour at each temperature be likewise plotted, it will be found that the points lie on a straight line (Fig. 16, dotted line), so that if S_m denotes the mean density at a temperature t, it may be written in the form—

$$S_m = S_0 + at.$$

This linear relation is known as the law of Cailletet and Mathias, or the law of the rectilinear diameter. It holds fairly accurately for a number of substances, though it must not be regarded as being strictly true in general. Thus for the case of isopentane, which has been most thoroughly examined from the standpoint of the continuity of state by S. Young (compare Young's *Stoichiometry*), it has been found that a more accurate relation is—

$$S_m = S_0 + at + \beta t^2.$$

Determination of the Critical Constants t_c, p_c, v_c.—The critical temperature and pressure may be obtained as follows: A bent tube

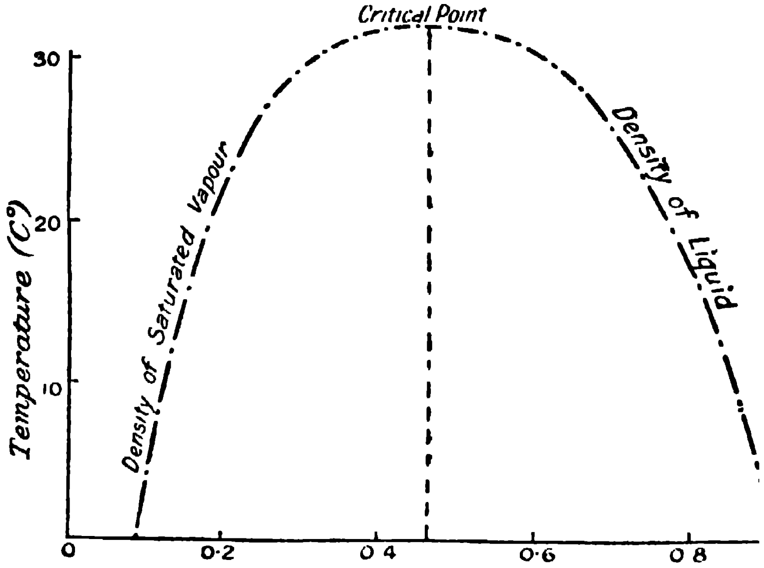


Fig. 16.

containing some of the liquid over mercury is placed in a heating bath and the temperature gradually raised (Fig. 17). In the case of carbon dioxide, Andrews (*Phil. Trans.*, Part II., p. 575, 1869; *ibid.*, Part II., p. 421, 1876) gives the following description of what takes place when the system consisting of liquid CO_2 in contact with saturated CO_2 vapour in a sealed tube, is gradually warmed to the region of 31° C.: " . . . the surface of demarcation of the liquid and gas became fainter, lost its curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass." Andrews called the temperature at which these phenomena appear the "critical point". The critical temperature is therefore that at which the surface of demarcation disappears, and this may be obtained directly from the temperature of the bath. Similarly from the difference in level of the mercury in the two limbs, the critical pressure may be read off directly. The critical volume might be read off directly from the observed volume, but the possibility of error is great because of the great compressibility of a substance at its critical point, whereby any slight alteration of pressure

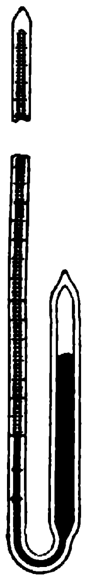


Fig. 17.—(From Young's *Stoichiometry*.)

has an enormous effect upon the volume. Young therefore recommends, as the most trustworthy means of obtaining the critical volume, the application of the law of Cailletet and Mathias, or rather the more accurate relation—

$$S_m = S_o + at + \beta t^2$$

which gives for the critical density S_c the expression—

$$S_c = S_o + a(t_c - t_o) + \beta(t_c - t_o)^2$$

in which S_c is simply $\frac{1}{v_c}$.

For further details of the experimental difficulties met with in the determination of critical values the reader is referred to Young's *Stoichiometry*.

Young (*Zeitsch. physik. Chem.*, **29**, 223, 1899) has collected a large amount of data in the case of isopentane, partly with the object of seeing how far the Cailletet-Mathias rule ($S_m = S_o + at$) holds good in this case. A few of his values are reproduced below.

ISOPENTANE.

Temperature Centigrade.	Density of Liquid.	Density of Vapour (Saturated).	Mean Density Observed.	Mean Density Calculated.
10	0·6295	0·0016	0·3156	0·3152
50	0·5881	0·0060	0·2970	0·2970
100	0·5278	0·0203	0·2741	0·2743
150	0·4445	0·0583	0·2514	0·2516
170	0·3914	0·0932	0·2423	0·2425
180	0·3495	0·1258	0·2378	0·2380
183	0·3311	0·1422	0·2366	0·2366
185	0·3142	0·1575	0·2358	0·2357
186	0·3028	0·1677	0·2353	0·2352
187	0·2857	0·1834	0·2346	0·2348
187·4	0·2761	0·1951	0·2356	0·2346
critical temp. 187·8		—	—	0·234

Critical volume of 1 gram $= \frac{1}{0{\cdot}234} = 4{\cdot}266$ c.c.

JAMES THOMSON'S EXTENSION OF ANDREWS' THEORY OF THE CONTINUITY OF STATE (*Proc. Roy. Soc.*, **20**, 1, 1871).

The following is a brief account of Thomson's theory as far as possible in his own words. Andrews showed that the ordinary gaseous and liquid states are only widely separated states of the same condition of matter, and may be made to pass the one into the other by a course of continuous physical changes representing nowhere any interruption or breach of continuity. The saturated vapour pressure curve or "boiling point" curve comes to an end at the critical point. "Now, it will be my [Thomson's] chief object in the present paper to state and support a view which has occurred to me, according to which it appears probable that, although there be a practical breach of continuity in crossing the line of boiling points from liquid to gas or from gas to liquid, there may exist in the nature of things, a theoretical continuity across this breach having some real and true significance. This theoretical continuity from the ordinary liquid state to the ordinary gaseous state must be supposed to be such as to have its various courses passing through conditions of temperature pressure and volume in unstable equilibrium for any fluid matter theoretically conceived as homogeneously distributed while passing through the intermediate conditions.

"It is first to be observed that the ordinary liquid state does not necessarily cease abruptly at the line of boiling points, as it is well known that liquids may, with due precautions, be heated considerably beyond the boiling temperature for the pressure to which they are exposed." Referring to Andrews' isothermals for CO_2—the p and v being the ordinates—Thomson points out that the system may still remain liquid under conditions in which it should consist partly of liquid and partly of vapour. Thus in the diagram (Fig. 18), the curve GA, which shows the volumes of the *liquid* under various pressures, does not necessarily change abruptly into AC when the point A is reached, but may extend *continuously* for some distance as is shown by the dotted line AB. Analogous behaviour may be observed in the case of the system when entirely gaseous, which decreases in volume as the pressure increases, so that the line HC is followed. On reaching C the system usually becomes partly liquid, that is, partial condensation occurs, the system now following the line CA. Under certain conditions, however, *e.g.* in the absence of condensation nuclei, the system remains gaseous, even on being compressed beyond C, so that the line HC continues unbroken to some point such as D, when in general sudden (partial) condensation occurs and the pressure and volume of the system corresponds to some point on CA.

Thomson considered that this idea of continuity might be extended so that a curve such as CDEFBA represents the hypothetical relations between p and v in place of the horizontal line AC. The part of the curve DEFB has never been realised experimentally. In spite of this, Thomson's view has the great advantage that since it substitutes a *continuous* curve in place of a discontinuous one, it renders possible the application of an *equation* which will reproduce the values of p and v for the liquid as well as for the gaseous state. (It is, of course, impossible to get an analytical expression which will correspond to discontinuous curves such as *actually* represent the relations between p and v below the critical point.) Thomson discusses these hypothetical isothermals as follows: "Let us suppose an indefinite number of curves each for one constant temperature to be drawn. . . . Now we can see, that as we pass from one curve to another in approaching toward the critical point *from* the *higher* temperatures, the tangent to the curve at the steepest point or point of inflexion is rotating [compare the curves for CO_2, Fig. 15, at the temperatures 48·1°, 35·5°, and 32·5° respectively], so that its inclination to the plane of the co-ordinate axes for pressure and temperature increases until at the critical point it becomes a right angle. Then it appears very natural to suppose that in proceeding onwards past the critical point to curves successively for lower and lower temperatures, the tangent at the point of inflection will continue its rotation, and the angle of its inclination, which before was acute, would now become obtuse. It seems much more natural to make such a supposition as this than to suppose that in passing the critical point from higher into lower temperatures, the curved line should break itself asunder and should come to have a part of its conceivable continuous course absolutely deficient. It thus seems natural to suppose that in some sense there is continuity in each of the successive curves, such as those drawn in the accompanying diagram as dotted curves uniting continuously the curves for the ordinary gaseous state with those for the ordinary liquid state."

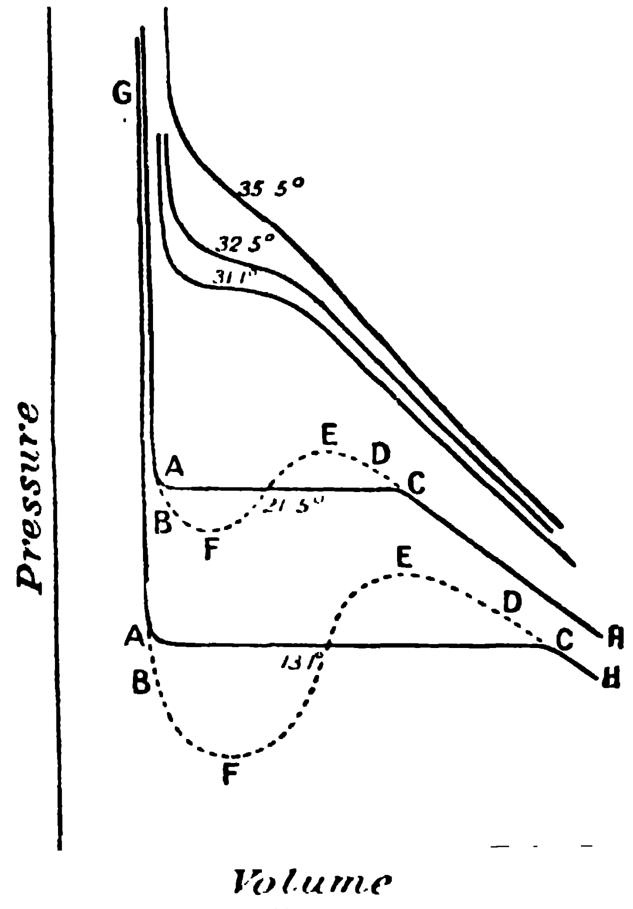


FIG. 18.

The dotted lines indicate on this CO_2 diagram Thomson's hypothetical isothermals.

Thomson says further: "The overhanging part of the curve from E to F seems to represent a state in which there would be some kind of unstable equilibrium; and so, although the curve there appears to have some important theoretical significance, yet the states represented by its various points would be unattainable throughout any ordinary mass of the fluid. It seems to represent conditions of co-existent temperature, pressure, and volume, in which, if all parts of a mass of fluid were placed, it would be in equilibrium, but out of which it would be led to rush partly into the rarer state of gas and partly into the denser state of liquid by the slightest inequality of temperature or of density in any part relatively to other parts."

ANALYTICAL EXPRESSIONS ("EQUATIONS OF STATE") PROPOSED TO REPRODUCE THE BEHAVIOUR OF GAS AND LIQUID SYSTEMS.

I. THE EQUATION OF RAMSAY AND YOUNG.

This expression applies only to the case in which the *volume of the system is kept constant.* The expression which gives a relation between the temperature and pressure under this condition may be written thus—

$$p = k\mathrm{T} - c$$

where p is the pressure exerted by the system,[1] k and c are constants to be determined by experiment, and T the absolute temperature. The relation may be expressed more generally thus—

$$p = \mathrm{T}f(v) - \mathrm{F}(v)$$

where f and F are different functions of the volume. If v is kept constant, $f(v)$ and $\mathrm{F}(v)$ are necessarily constants.

It will be seen that this equation is really a substitute for the Gay-Lussac expression (which states that $p = k\mathrm{T}$ when v is constant in the case of a perfect gas), the modification being the introduction of the term c. It is not, however (in the first form given), at the same time a substitute for Boyle's Law, so that the Ramsay and Young equation is necessarily limited in application, the constants k and c, for example, being only constant (by definition) as long as the system is kept at constant volume. For different volumes different numerical values must be assigned to k and c. Amagat (*Compt. Rend.*, **94**, 847, 1882) found that the relation held accurately for CO_2 and C_2H_4 for the gaseous state, but only approximately so for the liquid state. Ramsay and Young, on the other hand (*Phil. Mag.* [5], **23**, 435, 1887), found that the expression held good for ethyl ether for the liquid as well as for the gaseous state. Barnes came to the same conclusion, and Ramsay and Young showed further that the relation holds approximately for methyl, ethyl, and propyl alcohols, but that considerable discrepancies are observed in the case of water (see Ramsay and Young, *Phil. Mag.*, August, 1887; *Phil. Trans.*, A, **137**, 1889; *Phil. Trans.*, A, **107**, 1892). To show the applicability of the equation, we may take some of the data given by Ramsay and Young (*Phil. Mag.* [5], **23**, 435, 1887) in the case of ethyl ether. If the expression holds true, the pressure ought to be a linear function of the absolute temperature, the volume being kept constant. The diagram (Fig. 19) shows a number of the isochores thus obtained. An isochore is a curve on a pt diagram, the pressure and temperature being variable, the volume invariable. It will be observed that the curves are very nearly straight lines.

---

[1] The system considered must necessarily be homogeneous, either entirely liquid or entirely gaseous. This is true for all the "equations of state".

Another method of investigating the equation is to calculate the constants for any given volume. If we differentiate the expression with regard to T, we obtain—

$$\left(\frac{dp}{dT}\right)_v = k.$$

ISOCHORES FOR ETHER.

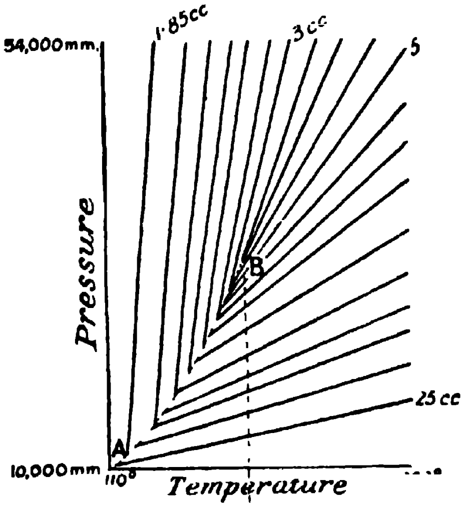


FIG. 19.

The Ramsay-Young Law. Isochores are practically straight lines. The dotted line AB represents saturated vapour pressures at various temperatures. To the left of this the system is liquid (small values of v); to the right the system is gaseous. The critical temperature marks the superior limit of the saturated vapour-liquid curve. The isochores are equally straight in liquid and vapour states, *i.e.* the Ramsay-Young Law applies to both states.

The value of $\frac{\partial p}{\partial T}$ is simply the tangent to the pt curve at any given temperature, and may thus be read graphically provided the data refer to constant volume. By substituting the value of k in the expression $p = kT - c$ for any two values of T and p (the volume being the same for both), one can solve for c. Having thus obtained k and c (corresponding to a given volume), values of p at other temperatures, but keeping the volume the same, may be calculated and compared with those observed. Other volumes may now be selected, and the corresponding k and c values obtained. By procedure such as this it is possible to see what are the limits of applicability of the law. The following table contains some of the data obtained by Ramsay and Young (*l.c.*) in the case of ether:—

ETHER AT 197° C., *i.e.* A FEW DEGREES ABOVE THE CRITICAL POINT.

Volume of 1 gram.	Pressure in mm. of Mercury.	Pressure Calculated by the R. and Y. Equation.
33·17	10108	10055
38·07	8972	8965
47·84	7312	7320
57·59	6166	6130
67·33	5356	5340
77·05	4718	4735
86·75	4219	4220
96·44	3820	3820

A more thorough investigation of the equation was undertaken by S. Young (*Zeitsch. physik Chem.*, **29**, 223, 1899) in the case of isopentane. The following values of $k = \left(\frac{dp}{dT}\right)_v$ are taken from the very extended tables given by Young.

(*a*) Volume of the system = 4·0 c.c., this being kept constant throughout the temperature range.

Temperature, Centigrade.	$k = \left(\frac{dp}{dT}\right)_v$.	Temperature, Centigrade.	$k = \left(\frac{dp}{dT}\right)_v$.
187·8 (critical)	405	210	443
190	418	220	439
195	428	230	462
200	434	240	446
205	430		

(*b*) Volume of system 50 c.c.

Temperature, Centigrade.	$\left(\frac{dp}{dT}\right)_v$.	Temperature, Centigrade.	$k = \left(\frac{dp}{dT}\right)_v$.
100	21·5	160	20·0
110	21·0	170	19·5
120	21·0	180	18·5
130	20·5	200	19·25
140	19·5	220	19·25
150	19·5		

(*c*) Volume of system = 3000 c.c.

Temperature, Centigrade.	$k = \left(\frac{dp}{dT}\right)_v$.	Temperature, Centigrade.	$k = \left(\frac{dp}{dT}\right)_v$.
30	31	70	28
40	31	80	31
50	29	90	32
60	27	100	29

Young says, "The values of $\left(\frac{dp}{dT}\right)_v$ are approximately but not completely constant. For volumes less than 4·6 c.c. the values of *k* increase with rising temperature, whilst at greater volumes the values decrease. At still greater volumes they appear to be constant."

The general conclusion is that the Ramsay and Young equation is very nearly but not quite in agreement with the actual behaviour of liquid and gas systems.

II. THE EQUATION OF VAN DER WAALS.[1]

This expression is wider in its scope than the first-quoted form of the Ramsay and Young equation in that it is proposed as a substitute for the entire "perfect gas" law $pv = \mathrm{RT}$, and is to be applicable to actual gases and liquids.

It is written thus—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT},$$

where *a* and *b* are regarded as constants characteristic of a given substance, but independent of temperature and volume, *p*, *v*, R, T, have their usual significance. The above expression differs from the perfect gas law in that it contains two correction terms, $\frac{a}{v^2}$ and *b*. The term $\frac{a}{v^2}$ is introduced to take account of the attractive forces between the molecules.[2] These forces are extremely great when the system is liquid, and although decreasing rapidly with temperature rise and rarefaction are still not negligible until the system is well above the critical point. The perfect gas law $pv = \mathrm{RT}$ assumes, of course, that there are no such *cohesive* forces operating between the molecules. In the interior of actual gases, vapours, and liquids, the cohesive forces which exist, say, upon a single molecule are mutually destructive because they are on the average exerted in all directions simultaneously. The existence of cohesion is shown when we consider a molecule near or at the surface. A molecule passing through the surface layer is retarded by the backwardly directed pull exerted upon it by the more interior molecules of the liquid, *i.e.* its impact, and therefore the pressure exerted by it is lessened owing to the cohesive forces. If such an imperfect gas or vapour exerts a pressure p against the walls of the containing vessel, the pressure which would be exerted by it if it obeyed Boyle's Law would be greater by a certain quantity π, *i.e.* the perfect gas under the same conditions would exert a pressure $(p + \pi)$. Van der Waals writes $\pi = \frac{a}{v^2}$. His reason for doing so is roughly as follows. The attractive or cohesive force between two volume elements of liquid is proportional to the product of the masses of each element, that is, is proportional to the product of the densities, or if the elements are similar, is proportional to the square of the density, and therefore proportional to $\frac{1}{v^2}$, since v varies inversely as the density. Assuming the proportionality factor to be a constant a—which depends of course on the chemical nature of the liquid, vapour, or gas considered, but is assumed to be independent of the temperature and volume of the system—we can write—

---

[1] J. D. van der Waals, *Dissertation*, Leyden, 1873; *Die Kontinuität des gasformigen und flussigen Zustands*, Teile I. u. II., Leipzig, 1899. There is also an English translation of the German edition of 1881 in the *Physical Society Memoirs*.

[2] It will be remembered that in the introductory chapter it has been shown that the van der Waals equation assumes the law of attraction to be the inverse fourth power of the distance between the molecules.

$$\text{cohesive force} = \frac{a}{v^2},$$

and hence the true pressure which ought to be exerted by the system is $(p + \frac{a}{v^2}$ where p is the *actual* pressure observed.[1]

Again, it is clear that in the actual case the molecules of a system must occupy some space. Hence if a gas be compressed to a high degree, the actual volume v may no longer be great compared with the least possible volume which would be reached when the molecules were made to touch. This limiting volume is denoted by b—van der Waals has shown that b is four times the actual effective volume of the molecules.[2] The *compressible* volume, *i.e.* the FREE space is thus $(v - b)$, and this is the quantity which should appear in any modified form of Boyle's Law, for this law does not take account of any volume occupied by the molecules themselves. [It is more than likely that the law governing the actual compressibility of the molecules themselves is entirely different from a simple one such as that of Boyle.] When we allow, therefore, for the simultaneous modification of the pressure and volume terms, the corrected expression, put in the shape of a "Boyle's Law," takes the form—

---

[1] The train of reasoning followed in the above paragraph in finding a basis for van der Waals' use of the square of the density may perhaps lead to a misunderstanding. The attraction between two molecules in all probability does not depend on the product of the masses of the molecules. We have already seen in Chap. I. that the attraction is essentially electrostatic and will therefore depend upon the charge carried by each doublet. The magnitude of the cohesion π will depend on the degree of packing of the molecules, that is upon their number in unit volume. It is this number which is proportional to the density, and it is in this way that the square of the density enters into the expression. Naturally as the number of molecules in a given volume element is increased the mass necessarily increases, but it is number of molecules and not their mass which is significant for molecular cohesion.

[2] See footnote to p. 13.

$$\left(p + \frac{a}{v^2}\right)(v - b) = k.$$

Now, if we simply make the *assumption* that the terms $\left(p + \frac{a}{v^2}\right)$ and $(v - b)$ should replace p and v in the general gas equation, we obtain—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}.$$

The above deduction of van der Waals' equation serves only to show the reasonableness of the modifications introduced. Van der Waals himself followed a more rigid method, starting from the Clausius virial.[1]

Van der Waals' expression is a cubic equation in v, as is seen when it is rewritten in the form—

$$v^3 - \left(b + \frac{\mathrm{RT}}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0.$$

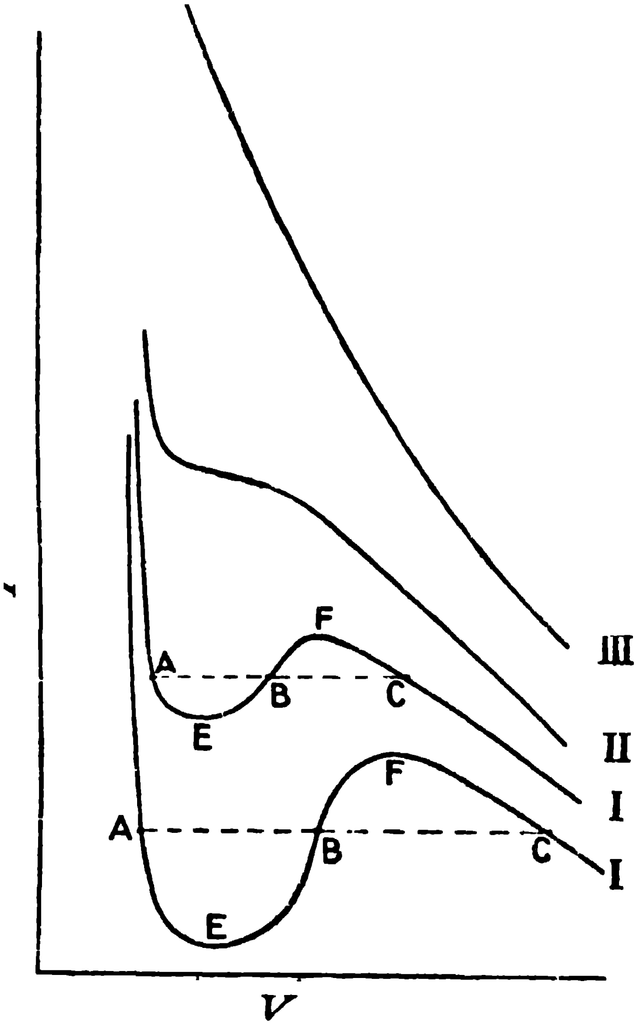
The equation has therefore three roots, *i.e.* three values of v for any given p and T, and further, all three roots may be real, or one real and two imaginary. The expression is therefore the equation of curves such as those shown in the diagram, Fig. 20.

When the roots are real and different, three different values for v (for a given p and T) are shown by the points A, B, and C, in curve I on the pv diagram. When the p and T values are such that the three roots are real and identical, the curve given by the equation is represented by II. When there is one real root and two imaginary, the curve has the shape represented by III. The resemblance between these curves and those suggested by James Thomson for the isothermals below, at, and above the critical point is very striking. The van der Waals equation carries out therefore this conception of the continuity of the liquid and gaseous states. It may also be pointed out that the equation predicts a similar continuity for the solid and liquid states, though in view of Tammann's work[2] this is very doubtful. It cannot be too strongly emphasised that the van der Waals equation applies only to a *homogeneous* system, *i.e.* a system entirely liquid or entirely gaseous. It cannot be applied directly to the case of liquid in contact with saturated vapour, as this system is heterogeneous, *i.e.* two-phase. To make it apply to the passage from gas to liquid, or *vice versâ*, we have to imagine the change to be continuous, that is, we have to imagine that, instead of the pressure remaining constant until liquefaction or vaporisation is complete, the pressure follows the curve AEBFC.

---

[1] The reader should consult van der Waals' monograph or Kuenen's *Die Zustandsgleichung*, in the "Wissenschaft" series.

[2] See G. Tammann's book, *Krystallisieren und Schmelzen*; see also Chwolson, *Lehrbuch der Physik*, vol. iii. pp. 583-4.



VAN DER WAALS ISOTHERMALS

FIG. 20.

CALCULATION OF THE CRITICAL CONSTANTS WITH THE AID OF VAN DER WAALS' EQUATION.

First Method.—At the critical point the three roots of the equation are identical, *i.e.* there is only one value for v, namely, the critical volume v_c, which will satisfy the equation when the pressure and temperature have the critical values p_c and T_c. As already mentioned, v_c, p_c, and T_c are the critical constants of the substance under examination.

It is possible to express them in terms of the van der Waals constants a and b in the following way:—

A cubic equation in v which possesses three identical roots may be written in the form—

$$(v - v_c)^3 = 0$$

where v_c is the root of the equation.

This expression when expanded in the ordinary way becomes—

$$v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0,$$

van der Waals' equation for the critical point being—

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{a}{p}v - \frac{ab}{p^c} = 0.$$

Now equating the coefficients of like powers of v in the two equations,[1] one obtains

$$3v_c = b + \frac{RT_c}{p_c} \quad . \quad . \quad . \quad . \quad (1)$$

$$3v_c^2 = \frac{a}{p_c} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$v_c^3 = \frac{ab}{p_c} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From these equations one can obtain the following values for v_c, p_c, and T_c, namely:—

$$v_c = 3b$$

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8}{27} \cdot \frac{a}{Rb}$$

and also

$$\frac{RT_c}{p_c v_c} = \frac{8}{3} = 2 \cdot 67.$$

If one determines, therefore, by experiment the pressures and volumes at various temperatures of the homogeneous liquid or gas, one can calculate a and b in the equation of state, and from these values the values of v_c, p_c, and T_c or *vice versâ*, a and b may be calculated by the above relations from the critical constants themselves.

Second Method.—The points E and F (Fig. 20) on the van der Waals isothermals below the critical point represent minima and maxima respectively. That is, at the point E the curve is such that $\frac{\partial p}{\partial v} = 0$, and $\frac{\partial^2 p}{\partial v^2}$ is positive. (Note that partial differentials are employed to denote that the temperature is constant.) Again, for the point F the curve is such that $\frac{\partial p}{\partial v} = 0$, and $\frac{\partial^2 p}{\partial v^2}$ is negative. At the critical temperature the points E and F coalesce. Hence for the critical isothermal we have the relations $\frac{\partial p}{\partial v} = 0$, and $\frac{\partial^2 p}{\partial v^2} = 0$. (Note that $\frac{\partial^2 p}{\partial v^2} = 0$, means that the tangent to the curve at the point of inflexion is horizontal.[1]) On rewriting van der Waals' equation in the form

---

[1] See, for example, Hall and Knights' *Algebra*, Chap. 35.

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

one obtains on differentiating with respect to v, keeping T constant—

$$\frac{\partial p}{\partial v} = \frac{-RT}{(v - b)^2} + \frac{2a}{v^3}.$$

Further differentiation gives—

$$\frac{\partial^2 p}{\partial v^2} = \frac{2RT}{(v - b)^3} - \frac{6a}{v^4}.$$

Hence at the critical point the following relations hold :—

$$\frac{-RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0, \quad \text{and} \quad \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0.$$

Dividing one expression by the other we obtain—

$$\frac{1}{2}(v_c - b) = \frac{1}{3}v_c$$

or

$$v_c = 3b \text{ as before.}$$

The values for p_c and T_c follow from this and take the form already given. This second method of examination has the advantage of being more general than the first, and is directly applicable to other equations of state.

CONNECTION BETWEEN VAN DER WAALS' EQUATION AND THE EQUATION OF RAMSAY AND YOUNG.

If we consider a homogeneous system—say a gas—which is kept at constant volume whilst undergoing pressure changes due to changes in temperature, the equation of van der Waals may be simplified thus. The term $\frac{a}{v^2}$ is now a constant, and may be denoted by c; $(v - b)$ can also be regarded as a constant, say c_1, so that the equation becomes—

$$(p + c)c_1 = RT$$

or, denoting $\frac{R}{c_1}$ by k,

$$p + c = kT$$

or

$$p = kT - c$$

---

[1] At higher temperatures there is still a point of inflexion, but $\frac{\partial^2 p}{\partial v^2}$ is no longer zero. Finally, at still higher temperatures the inflexion vanishes.

which is the Ramsay-Young equation. The van der Waals equation will therefore give rise to the same type of isochores as those given by the Ramsay-Young expression. The connection between the equations may also be observed if we write the Ramsay-Young expression in the form—

$$p = \mathrm{T}f(v) - \mathrm{F}(v)$$

and the van der Waals expression in the form—

$$p = \frac{\mathrm{RT}}{v - b} - \frac{a}{v^2}.$$

They are identical on the assumption that—

$$f(v) = \frac{\mathrm{R}}{v - b} \text{ and } \mathrm{F}(v) = \frac{a}{v^2}.$$

Van der Waals equation is therefore a special case of the general Ramsay-Young equation for systems at constant volume.

APPLICATION OF VAN DER WAALS' EQUATION TO SOME ACTUAL CASES.

Van der Waals' himself gives the following calculations based on Andrews' data for carbon dioxide. The object is to see if a and b are really constant. The two terms occur, of course, simultaneously, and if there be variation in one it will not be possible to eliminate the effect from the other. Employing the same units for p and v as those of Andrews, van der Waals has calculated a to be 0·008704 for CO_2 gas. Taking this to be correct, the following table indicates the values of b calculated from the equation in the case of CO_2:—

	Temperature 13·1° C.		Temperature 21·5° C.	
	v.	b.	v.	b.
CO_2 entirely gaseous	0·013764	0·00242	0·016044	0·00241
	0·013036	0·00234	—	—
	0·012933	0·002399	—	—
CO_2 entirely liquid	0·0022647	0·001663	0·002935	0·001924
	0·0022234	0·001643	0·0024526	0·001734
	0·0021822	0·001627	0·0024288	0·001719
	0·0020937	0·001585	—	—
	0·0020527	0·001565	—	—

Temperature 35·5° C. (above the critical point. System therefore entirely gaseous).

v.	b.	v.	b.
0·01367	0·0025	0·007016	0·0025
0·012716	0·0025	0·00496	0·00234
0·01173	0·0027	0·00321	0·0020
0·0106	0·0025	0·003026	0·00195
0·00955	0·00244	0·00275	0·00184
0·00837	0·00254	0·002629	0·001798

It will be seen from the above data that b is *not* constant. It decreases as v decreases, *perhaps* due to a slight compressibility on the part of the molecules themselves, though this can hardly be regarded as the whole cause. There is evidence also—although not shown clearly by the data quoted—that b increases slightly with rise in temperature. The data show, however, that on the whole the equation expresses with considerable approximation the behaviour of gaseous and liquid systems. The degree of applicability will be more clearly realised when it is remembered that although the term a/v^2, which is the cohesive or "internal"—or "intrinsic"—or "molecular"—pressure term, varies from a few atmospheres in the gaseous state to over 1000 atmospheres[1] for the liquid state in the case of carbon dioxide, yet the value of b varies within moderate limits.

It will be of interest to see how far the equation applies to another case, namely, ethylene. From the values of v_c, p_c, and T_c experimentally obtained, van der Waals calculated a to be 0·00786 and b to be 0·00224. Assuming these to be constants, the following values of the products (pv) were calculated by Baynes (*Nature*, **22**, 186, 1880):—

ETHYLENE AT 20° C.

p in Atmospheres.	(pv) Observed by Amagat.	(pv) Calculated from van der Waals' Equation.
1	1000 (in arbitrary units)	1000
31·58	914 ,, ,,	895
72·9	416 ,, ,,	387
84·16	399 ,, ,,	392
110·5	454 ,, ,,	456
176·01	643 ,, ,,	642
233·58	807 ,, ,,	805
282·21	941 ,, ,,	940
329·14	1067 ,, ,,	1067
398·71	1248 ,, ,,	1254

---

[1] APPROXIMATE VALUES OF THE INTERNAL PRESSURE OF LIQUIDS.

The following are the values obtained by van der Waals in the case of a few *liquids* at 0° C. approximately:—

Ethyl ether, 1300 atmospheres.
Ethyl alcohol, 2100 ,,
Carbon disulphide, 2900 atmospheres.
Water, 10,500 atmospheres

For further values, see a paper by W. C. McC. Lewis, *Trans. Faraday Soc.*, 1911.

The two columns of figures agree fairly well. A more complete examination of the equation has shown, however, that in no case can *a* or *b* be regarded as absolutely constant, and hence, although the van der Waals equation gives an approximate solution, it is recognised that its applicability is not rigid. These conclusions appear more clearly from considerations such as the following:—

COMPARISON OF THE RATIO OF RT TO *pv* AT THE CRITICAL POINT AS GIVEN BY THE EQUATION AND THAT ACTUALLY OBSERVED.

If one substitutes in the ratio $\frac{RT}{p_c v_c}$ the values of the critical constants p_c, v_c, and T_c, as given by the van der Waals equation, it is found that the ratio simply reduces to the quantity $\frac{8}{3}$ or 2·67, which should therefore be the same for *all* substances. It will be seen that the above ratio is identical with the ratio between the value of *pv* for a perfect gas (since this is RT) and the value of *pv* for an actual gas. (In other words, 2·67 is the ratio of the density of a gas obeying van der Waals' equation to that of a perfect gas at the same (critical) temperature and pressure.)

The following data (selected mainly from S. Young's paper, *Proc. Roy. Dub. Soc.*, **12**, 374, 1910) show the experimentally determined values of the ratio $\frac{RT_c}{p_c v_c}$ for a number of substances:—

Substance.	$\frac{RT_c}{p_c v_c}$.
Helium	3·13[1]
Argon	3·283[1]
Xenon	3·605[2]
Oxygen	3·346[3]
Ethylene	3·42
n. pentane	3·766
n. hexane	3·831
n. heptane	3·854
n. octane	3·865
Isopentane	3·735
Hexamethylene	3·706
Benzene	3·755
Fluorobenzene	3·796
Chlorobenzene	3·776
Bromobenzene	3·809
Iodobenzene	3·780
Carbon tetrachloride	3·680
Zinc chloride	3·740
Ethyl ether	3·813
Methyl formate	3·922
Ethyl formate	3·895
Methyl acetate	3·943
Ethyl acetate	3·949
Methyl butyrate	3·903

---

[1] Onnes, *Proc. Roy. Acad. Amsterdam*, 1911.

[2] Patterson, Cripps, and R. Whytlaw-Gray, *Proc. Roy. Soc.*, A, **86**, 579, 1912.

[3] Onnes, *Proc. Roy. Acad. Amsterdam*, 1911.

Substance.	$\frac{RT_c}{p_c v_c}$
Carbon dioxide	3·620
Sulphur dioxide	3·830
"*Abnormal Substances.*"	
Methyl alcohol	4·559
Ethyl alcohol	4·026
Propyl alcohol	3·998
Acetic acid	4·992

It will be observed that the experimentally found value for the ratio $\frac{RT_c}{p_c v_c}$ is nearly a constant for a large number of substances as van der Waals' equation predicts, but the actual numerical value is approximately $\frac{4}{3}$ times as great as the theoretical value (2·67). This is of course a very serious discrepancy, and up to the present no satisfactory explanation of it is forthcoming. It may be pointed out that the mean experimental value indicates that the actual density for the above "normal" substances at their critical points is approximately 3·7 times the density of a perfect gas. Note that the monatomic gases, argon and xenon—which from their simple structure might be expected to approximate most closely to van der Waals' equation—show much the same discrepancy as other substances whose molecules are much more complex.

BEHAVIOUR OF MATTER AT EXTREMELY HIGH PRESSURES.

According to van der Waals' equation the critical volume $v_c = 3b$ or $b = \frac{v_c}{3}$. If a substance be compressed a limit is theoretically reached when the volume becomes equal to b, that is, to $\frac{v_c}{3}$. It has been found, however, that in the actual cases the limiting volume is approximately $\frac{v_c}{4}$, *i.e.* matter is more compressible than is predicted by the equation. This "found" limit is obtained by extrapolation of the Cailletet-Mathias mean density line to the temperature T = 0° absolute, at which point the density of the vapour is zero and the actual density of the liquid is double the value given by the mean density line. In this way Guldberg, and later D. Berthelot (*Archives Néerlandaises* (2), **5**, 446, 1900) found the following values for the limiting specific volumes of various substances:—

O_2	Cl_2	CO_2	SO_2	C_2H_4
0·278v_c	0·282v_c	0·269v_c	0·243v_c	0·243v_c
	CCl_4	$C_4H_{10}O$	C_6H_6	
	0·260v_c	0·255v_c	0·258v_c	

The mean of these values is 0·26v_c, the value given by van der Waals' equation being 0·33v_c.

ACCURATE DETERMINATION OF MOLECULAR WEIGHTS OF GASES.

Berthelot (compare Kuenen, *Die Zustandsgleichung* (Wissenschaft Series)), has modified van der Waals' equation somewhat, and has employed the resulting expression in place of the perfect gas law in order to determine with a high degree of accuracy the molecular weights of gases from density determinations. The method is discussed in a number of papers in the *Journal de chimie physique.*

THE VARIATION OF THE PRODUCT *pv* WITH *p* FROM THE STANDPOINT OF VAN DER WAALS' EQUATION.

In the diagrams (Figs. 10 to 14) it has been shown that the isothermal variation of the product pv with p passes through a minimum, except in the case of hydrogen, at ordinary temperatures. The position of the minimum alters with the temperature, a series of such minima in the case of CO_2 being represented in Fig. 14 by the longer dotted line. It will be observed that this is parabolic in shape, and may be extrapolated on the upper side until it cuts the pv axis. This simply means that at and above a certain temperature the isothermal pv, p curves on the diagram will be similar to those of hydrogen at ordinary temperatures, since the minimum is now shifted over to the axis. Let us consider this state of things, namely, that the system is just at the temperature at which the minimum point is on the pv axis. For *any* of the minimum points indicated by the dotted line (Fig. 14) the following relation necessarily holds:—

$$\frac{\partial(pv)}{\partial p} = 0.$$

Now, according to van der Waals—

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

and therefore

$$pv = \frac{RTv}{v - b} - \frac{a}{v}.$$

Hence

$$\frac{\partial(pv)}{\partial p} = \left\{\frac{RT(v - b - v)}{(v - b)^2} + \frac{a}{v^2}\right\}\frac{\partial v}{\partial p} = \left\{\frac{-bRT}{(v - b)^2} + \frac{a}{v^2}\right\}\frac{\partial v}{\partial p}.$$

It is not necessary to work out the expression for $\frac{\partial v}{\partial p}$. It is clear that it will have a real value, not zero. The above expression for $\frac{\partial(pv)}{\partial p}$ will, therefore, be zero, *i.e.* there will be a minimum point on the curve when

$$\frac{(v - b)^2}{v^2} = \frac{b}{a}RT.$$

This relation holds good as a criterion of any of the minima. Now consider the special case of the minimum point being just on the pv

axis. Suppose the temperature is T_1. Since $p = 0$, $v = \infty$. Hence the above relation becomes—

$$\frac{b}{a}RT_1 = 1, \text{ or } RT_1 = \frac{a}{b}.$$

Now if we write a and b in terms of the critical temperature of the gas, we have the following equations:—

$$RT_c = \frac{8}{27}\frac{a}{b}$$

and therefore—

$$T_1 = \tfrac{27}{8}T_c = 3{\cdot}375T_c$$

According to van der Waals' equation, therefore, the temperature, at which the minimum value of pv on the $(pv)p$ sets of curves is found just on the pv axis, should be 3·375 times the critical temperature of the gas—no matter what the gas may be. Let us compare this with experiment. Employing the data of Amagat in the case of CO_2, the value for T_1 is found to be 636° C., or 909° abs., whilst the critical temperature is 304° abs. The ratio is 2·98. Other gases have been examined (Leduc and Sacerdote, *Compt. Rend.*, **124**, 285, 1897), and the ratio in these cases is also approximately 2·98. We see once more, therefore, that the van der Waals' equation, whilst correctly predicting the general behaviour and relations, breaks down in the quantitative conclusions.

THE PRINCIPLE OF CORRESPONDING STATES.

Consider the van der Waals' equation—

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

for any given homogeneous substance—either liquid or gas. Let us express the p, v, and T as multiples or submultiples of the critical values p_c, v_c, and T_c; that is, let us write—

The actual pressure p as πp_c
" volume v " ϕv_c
" temperature T " θT_c.

Substituting these values in the above equation, we obtain—

$$\left(\pi p_c + \frac{a}{\phi^2 v_c^2}\right)(\phi v_c - b) = R\theta T_c.$$

If we write now the values of a, b, and R likewise in terms of the critical constants (p. 75), the equation takes the form—

$$\left(\pi p_c + \frac{3p_c v_c^2}{\phi^2 v_c^2}\right)\left(\phi v_c - \frac{v_c}{3}\right) = \frac{8}{3}\frac{p_c v_c}{T_c} \cdot \theta T_c$$

which reduces to

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$

an expression which does not contain the characteristic constants *a* or *b* for any particular substance. This equation, written in conformity with the recommendations of the "International Commission" takes the form—

$$\left(p_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r.$$

This equation is known as the *reduced equation of state*, and should apply equally to all substances. In other words, if we consider any two substances whatsoever, either in the liquid or in the gaseous form, and suppose that we choose the temperature of each substance so that each temperature is the same fraction of the respective critical temperature, and if we bring the pressure of each substance to the same fraction of the respective critical pressure, then it will be found that the volume of each substance is the same fraction of the respective critical volume for each.

When the pressures exerted by any two substances are the same fraction of the respective critical pressures, the substances are said to be at *corresponding pressures*. An analogous definition holds for the terms *corresponding temperature* and *corresponding volume*. When any two of the variables p, v, T are fixed for a series of substances in such a way that the values are corresponding values, then, as shown above, the third variable will also be found to correspond for the various substances, and the substances are said to be in *corresponding states*.

We may now consider some experimental data collected by S. Young for the purpose of investigating this principle. The systems were selected so that the ratio π or p_r of the actual pressures of the various substances to the respective critical pressures is the same for all, and has the value 0·08846. At the same time, the temperatures were chosen so that the ratio θ or T_r of the absolute temperatures to the respective critical temperatures was the same for all, namely, 0·73 to 0·74. The following table shows the value of ϕ or v_r, the ratio of the actual specific volumes to the respective critical volumes. The substances are all examined under *corresponding* conditions with respect to temperature and pressure, and, therefore, if the principle of corresponding states is true, the observed volumes should likewise be at corresponding values, *i.e.* v_r should be the same for all. It will be observed that the temperatures and pressures happen to be so chosen that the substances can exist both in the liquid and in the vapour state. There are, therefore, two series of specific volumes to be taken into account, namely, v_{liquid} and v_{gas}, corresponding to the end points of the horizontal line in the pv diagram. According as we consider the homogeneous liquid or homogeneous gaseous state, there is a different numerical value to be assigned to the ratio of the actual to the critical volume for such substance. There are, therefore, two columns of figures in the table. The principle of corresponding states would, however, lead us to expect that if we compare liquids throughout or gases throughout the values of v^r should be the same for all substances, since each system has previously been brought to the same p_r and T_r.

SUBSTANCES IN CORRESPONDING STATES (data taken from portion of table in Young's *Stoichiometry*, p. 219).

$p_r = 0{\cdot}08846$. $T_r = 0{\cdot}73$ to $0{\cdot}74$.

	Substance.	$\frac{v_{\text{liquid}}}{v_c} = v_{r_1}$.	$\frac{v_{\text{gas}}}{v_c} = v_{r_2}$.
	Benzene	0·4065	28·3
	Isopentane	0·4085	27·7
	n. Pentane	0·4061	28·4
	n. Hexane	0·4055	29·1
	Fluorbenzene	0·4067	28·4
	Chlorbenzene	0·4028	28·5
	Carbon tetrachloride	0·4078	27·45
	Ethyl ether	0·4030	28·3
	Methyl formate	0·4001	29·3
	Ethyl formate	0·4003	29·6
$T_r = 0{\cdot}77$ approximately.	Methyl acetate	0·3989	30·15
	Acetic acid	0·4100	25·1
	Methyl alcohol	0·3973 approx.	34·35
	Propyl alcohol	0·4002 ,,	30·85
	Ethyl alcohol	0·4061 ,,	32·15

The principle of corresponding states is thus in agreement with experience, although it is noticeable that the correspondence is better the more closely the substances are related chemically.

It is of importance to notice that the conclusion to which one has come on the basis of the van der Waals' equation in regard to the existence of corresponding states does not necessarily stand or fall with the applicability or inapplicability of the equation itself. It is quite conceivable that other equations would also predict the existence of corresponding states. It will be done, in fact, by any equation containing three constants, *i.e.* as many constants as there are variables, p, T, and v. In van der Waals' equation the three constants are a, b, and R. The principle of corresponding states would not be predicted by an equation such as that of Clausius, which will be considered next, since this contains four constants, a, b, c, and R, unless some connection exists between a pair of these constants themselves.

Two methods (due to Amagat and Raveau respectively) of testing the reduced equation of state are given by Kuenen (*Die Zustandsgleichung*, pp. 84-86), also Young's *Stoichiometry*, pp. 215 *seq.* It has been found that the equation corresponds very closely to experiment in regions well above the critical point, but shows considerable discrepancies in the neighbourhood of this point.

III. The Equation of Clausius.

We have seen that the terms a and b in van der Waals' formula are not absolute constants, since they vary with temperature and volume. Clausius (*Wied. Ann.*, **9**, 337, 1880) suggested, therefore, that the term a/v^2 should be replaced by the term $\frac{a}{(v+c)^2} \cdot \frac{1}{T}$. In this expression it is assumed that the cohesive force varies inversely as the absolute temperature. c is a constant, characteristic of the substance under examination. The Clausius equation is, therefore—

$$\left\{p + \frac{a}{T(v+c)^2}\right\}(v - b) = RT.$$

We now proceed to test the applicability of this equation.

By applying the usual criteria for the critical point, namely, that $\frac{\partial p}{\partial v} = 0$, and $\frac{\partial^2 p}{\partial v^2}$ 0, one finds the relations—

$$\frac{-RT_c}{(v_c - b)^2} \quad \frac{2a}{T_c(v_c + c)^3} = 0,$$

and

$$\frac{2RT_c}{(v_c - b)^3} - \frac{6a}{T(v_c + c)^4} = 0.$$

From these one deduces the following values for the critical constants:—

$$v_c = 3b + 2c$$

$$\frac{p_c}{RT_c} = \frac{1}{8}\frac{1}{b + c}$$

$$RT_c^2 = \frac{8}{27}\frac{a}{b + c}.$$

It will be observed that the Clausius equations contain four constants, a, b, c, and R. The principle of corresponding states (which is borne out fairly completely by experience) requires, as we have seen, a *three*-constant formula. In order to be able to predict the principle of "correspondence" from the Clausius equation it is necessary to assume that c is a function of b, and this function must be the same for all substances. Thus, according to the principle, the expression $\frac{RT_c}{p_c v_c}$ should be the same for all substances. From the above relations it will be seen that—

$$\frac{RT_c}{p_c v_c} = \frac{8(b + c)}{3b + 2c},$$

and this can only be constant when b and c are proportional to one another. Thus, if $c = kb$, then

$$\frac{RT_c}{p_c v_c} = \frac{8(1 + k)}{3 + 2k}$$

where k is supposed to have the same value for all substances—a pure assumption.

Further, let us apply Clausius' equation to the pv, p diagram. The temperature which has been denoted by T_1, namely, that at which the minimum point of the pv curve lies just on the pv axis (*i.e.* $v = \infty$, $p = 0$), was defined according to the van der Waals equation by the relation $RT_1 = \frac{a}{b}$. The Clausius equation gives the relation $RT_1^2 = \frac{a}{b}$. Substituting the values of a and b obtained from the critical data, *viz.*—

$$RT_c^2 = \frac{8}{27}\frac{a}{b + c} = \frac{8}{27}\frac{a}{b(1 + k)}$$

we obtain
$$T_1^2 = T_c^2 \frac{27}{8}(1 + k),$$

or
$$T_1 = T_c \quad \frac{27}{8}(1 + k).$$

Now, we saw by *experiment* that $T_1 = 2{\cdot}98T_c$ on the average; and in order to obtain this numerical relation from the above expression it is necessary to write $k = 1{\cdot}631$.

Employing this value for k we find that—

$$\frac{RT_c}{p_cv_c} = \frac{8(1 + k)}{3 + 2k} = 3{\cdot}$$

This value is nearer the actual mean experimental value, $3{\cdot}7$, than the value given by van der Waals' equation ($2{\cdot}67$), but it is still too low. That is, the Clausius equation is also not exact. The equation has been found, further, to break down when examined in other directions, and for these reasons we need not further consider it, especially as it has the disadvantage of containing one arbitrary constant in addition to those analogous to the van der Waals constants without possessing a correspondingly greater degree of applicability.

IV. The Equation of Dieterici.

C. Dieterici (*Ann. der Physik* [4], **5**, 51, 1901) has suggested the following expression:—

$$p(v - b) = RTe^{\frac{A}{RTv}}$$

where e is the base of natural logarithms, b has the same significance as in van der Waals' equation, and is treated in the first instance as a constant. The term A is a constant characteristic of the cohesion pressure. The general considerations upon which the above expression is based may be briefly stated.

In the interior of a gas whose molecules possess cohesive force it may be assumed that since the cohesion is effective in all directions simultaneously, the translatory movements of the molecules will not be affected by it, and the pressure P_1 in the interior would be accurately given on the basis of the kinetic theory of gases. The actual pressure exerted upon the boundary or walls of the enclosing vessel will be smaller than P_1, because of the effective pull towards the interior exerted upon the molecules at the surface. On these grounds, therefore, we see that (1) the *number* of molecules which reach the boundary per second is smaller than those reaching an imaginary plane in the interior, because some of the molecules will possess too little velocity to reach the boundary at all, *i.e.* they will possess too little kinetic energy to overcome the backward pull; and (2) those molecules which do reach the boundary have lost some of their kinetic energy in overcoming the backward pull, and will therefore possess less momentum, and hence exert a smaller pressure than the same number would exert in the interior. Hence, if one denotes by A the work—reckoned per unit mass of the gas—done against the cohesive pull, the actual pressure p exerted by the gas at the boundary will be given by the expression—

$$p = P_1 e^{-\frac{A}{RT}}$$

But $P_1 = \frac{RT}{v - b}$, which is the ordinary gas equation, in which, however, the molecules are not regarded as points but as occupying a certain volume, such modification being represented by the b term. Substituting this relation in the first equation, one obtains—

$$p = \frac{RT}{v - b} e^{-\frac{A}{RT}}$$

or
$$\frac{A}{RT} = \log_e \frac{RT}{p(v - b)}.$$

Dieterici found, however, that the values thus given for A varied with the volume in the sense that A diminished as v increased. He therefore replaced the term $\frac{A}{RT}$ by $\frac{A}{RTv}$, thus obtaining the equation—

$$p = \frac{RT}{v - b} . e^{-\frac{A}{RTv}}.$$

Dieterici showed that this equation will yield the following results: (1) A maximum and minimum value for p as in the case of isothermals on the pv diagram below the critical point (compare the theoretical isothermals of van der Waals, Fig. 20, or of James Thomson, Fig. 18); (2) that at a certain temperature the equation gives a pressure curve on the pv diagram which contains a point of inflection, *i.e.* the critical isothermal; and (3) that at higher temperature the curves for p show neither a maximum nor minimum,[1] and thus correspond to the actual shape of isothermals above the critical point. These conclusions can be shown as follows: Let us differentiate the expression with respect to v, temperature being kept constant and b being likewise regarded as a constant. The condition for a maximum or minimum point on the pv curve is that $\frac{\partial p}{\partial v} = 0$, that is, writing $\frac{A}{RT}$ as a constant c, one obtains the relation—

$$-\frac{RT}{(v-b)^2} \cdot e^{-\frac{c}{v}} + \frac{RT}{v-b} e^{-\frac{c}{v}} \times \frac{c}{v^2} = 0,$$

whence
$$\frac{c}{v^2} = \frac{1}{v-b}$$

or
$$v = \frac{c}{2}\left(1 \pm \sqrt{1 - \frac{4b}{c}}\right).$$

When c is greater than $4b$ there are two values of v at which $\frac{\partial p}{\partial v} = 0$, that is, at which p has either a maximum or minimum value. This corresponds to the James Thomson isothermals below the critical point. When c is equal to $4b$ the roots of the equation are identical. This corresponds to the critical isothermal. When c is less than $4b$ the roots are imaginary. In other words, there is no real value of v for which $\frac{\partial p}{\partial v} = 0$, *i.e.* for which p is a maximum or minimum. This is the case for isothermals above the critical point. We thus see that, qualitatively at least, this equation is in agreement with the general idea of continuity of state.

Further, it will be observed that the equation contains three constants. It is therefore in agreement with the principle of corresponding states.

Now let us calculate the values of the critical constants, T_c, p_c, v_c, in terms of the Dieterici constants. As we have already seen, the criteria of the critical point are represented by the relations—

$$\frac{\partial p}{\partial v} = 0, \text{ and } \frac{\partial^2 p}{\partial v^2} = 0.$$

Carrying out this differentiation of the Dieterici expression, one obtains two equations by means of which the following relations may be deduced:—

$$v_c = 2b$$
$$RT_c = \frac{A}{4b}$$
$$p_c = \frac{A}{4b^2} \cdot e^{-2}.$$

---

[1] The curves may still show an inflection point, but $\frac{\partial^2 p}{\partial v^2}$ is only zero at the critical point, *i.e.* the tangent is horizontal only at T_c

From these it follows at once that—

$$\frac{RT_c}{p_c v_c} \cdot \tfrac{1}{2}e^2 = 3{\cdot}695,$$

a value which is in very good agreement with the average experimental figures, pp. 79, 80. On this particular point, therefore, the Dieterici equation is in much closer agreement with experiment than is the equation of van der Waals.

For the case of the critical isothermal, the Dieterici equation can be written—

$$p = \frac{RT_c}{v - b} e^{-\frac{A}{RT_c v}},$$

and on substituting the critical constants in place of A and b the equation becomes—

$$p = \frac{RT_c}{v - \frac{1}{2}v_c} \cdot e^{-\frac{2v_c}{v}}.$$

To show the agreement between theory and experiment, this expression has been applied to the calculation of the critical isothermal in the case of isopentane.

CRITICAL ISOTHERMAL OF ISOPENTANE.

$T_c = 460{\cdot}8.$ $v_c = 4{\cdot}266$ c.c.

v in c.c.	p Calculated (mm. Mercury).	p Observed (mm. Mercury).	v in c.c.	p Calculated (mm. Mercury).	p Observed (mm Mercury).
2·4	42,730	49,080	8	23,400	23.710
2·5	35,810	40.560	10	21,590	22,040
2·6	32,090	34,980	12	19,850	20,300
2·8	28,390	28,940	15	17,540	17,980
3·0	26,780	26,460	20	14,560	14,840
3·2	26,000	25,490	30	10,770	10,950
3·6	25,420	25,050	40	8,508	8,570
4·0	25,320	25,020	50	7,025	7,068
4·3	25,300	25,005	60	5.978	6.001
4·6	25,300	25,000	80	4,604	4,614
5·0	25,240	24,940	90	4,127	4,132
6·0	24,880	24,840	100	3,740	3,750

Except in the case of the smallest volumes (high pressure region) the agreement between calculation and experiment is within 1 to 2 per cent. Dieterici concludes that the discrepancies which do exist are due to the fact that b is not quite constant, but is a function of v.

The most serious drawback, however, to Dieterici's equation is the fact that it yields the relation $v_c = 2b$. When p is infinitely great the limiting volume becomes identical with b, and therefore, according to Dieterici, identical with $\frac{1}{2}v_c$. It has been already shown experimentally, however (p. 80), that the limiting volume is more nearly $\frac{1}{4}v_c$.

Dieterici's equation shows therefore an even greater discrepancy as regards this quantity than does the equation of van der Waals, according to which the limiting volume is $\frac{1}{3}v_c$.

The equation of Dieterici may be put in a somewhat different and at the same time more general form if the term T be raised to the nth power, n being characteristic of the substance under investigation. The expression is then—

$$p = \frac{RT}{v - b}e^{-\frac{a}{T^n v}}.$$

By differentiation it follows that—

$$\frac{\partial \log p}{\partial v} = \frac{1}{p}\frac{\partial p}{\partial v} = -\frac{1}{v - b} + \frac{a}{T^n v^2}$$

and $$\frac{\partial}{\partial v}\left(\frac{\partial \log p}{\partial v}\right) = \frac{1}{p}\frac{\partial^2 p}{\partial v^2} - \frac{1}{p^2}\left(\frac{\partial p}{\partial v}\right)^2 = \frac{1}{(v - b)^2} - \frac{2a}{T^n v^3}.$$

At the critical point each of these expressions is zero; that is—

$$\frac{1}{v_c - b} = \frac{a}{T_c^n v_c^2} \text{ and } \frac{1}{(v_c - b)^2} = \frac{2a}{T_c^n v_c^3}.$$

Whence $$v_c = 2b,$$

$$T_c^n = \frac{a}{4b},$$

$$p_c = \frac{R\left(\frac{a}{4b}\right)^{\frac{1}{n}} . e^{-2}}{b},$$

and $$\frac{RT_c}{p_c v_c} = \frac{(v_c - b)}{v_c}e^2 = \frac{1}{2}e^2 = 3{\cdot}69 \text{ as before.}$$

The Variation of pv with p from the Standpoint of the General Dieterici Equation.

The general Dieterici equation yields the following expression for pv:—

$$pv = \frac{RTv}{v - b}e^{-\frac{a}{T^n v}}.$$

Hence $$\log (pv) = \log RT + \log v - \log (v - b) - \frac{a}{T^n v},$$

or $$\frac{1}{pv}\frac{\partial(pv)}{\partial p} = \left(\frac{1}{v} - \frac{1}{v - b} + \frac{a}{T^n v^2}\right)\frac{\partial v}{\partial p}.$$

The minimum point for each isothermal on the pv, p diagram is given by the relation—

$$\frac{1}{pv}\frac{\partial}{\partial p}(pv) = 0,$$

and since $\frac{\partial v}{\partial p}$ is not zero, it follows that this condition is satisfied when—

$$\frac{1}{v} - \frac{1}{v-b} + \frac{a}{T^n v^2} = 0,$$

or

$$T^n = \frac{a}{b}\left(1 - \frac{b}{v}\right).$$

For the particular case in which the minimum of the curve lies just on the pv axis (*i.e.* $p = 0$ and $v = \infty$), the temperature T_1 is given by the last equation in the form—

$$T_1{}^n = \frac{a}{b}.$$

On substituting the critical constants for a and b, one finds

$$\frac{T_1{}^n}{T_c{}^n} = 4 \text{ or } T_1 = T_c\sqrt[n]{4}.$$

Now it has been pointed out, in discussing the van der Waals equation, that the experimental value of the ratio $\frac{T_1}{T_c}$ is 2·98 for a number of gases (whether this is really a constant or not is still undecided). To make the above relation conform to this it is necessary to write $\sqrt[n]{4} = 2{\cdot}98$, whence $n = 1{\cdot}27$.

If we regard this number as a constant *independent of the nature of the gas*, the general form of the Dieterici equation is likewise a three-constant one, and therefore the number of constants (a, b, and R) is equal to the number of variables (p, v, and T), and a "reduced equation" can be written down containing quantities independent of the nature of any particular substance, and therefore in agreement with the principle of corresponding states. It will be observed that the first equation of Dieterici is a three-constant one as it stands.

Many other equations of state have been proposed, but the brief survey given of those of Ramsay and Young, van der Waals, Clausius, and Dieterici respectively is sufficient to indicate the nature of the problem and the limitations exhibited by each. No equation altogether satisfactory has yet been proposed; that is, in no case are the "constants" quite independent of temperature and volume. We shall return to these equations later from the standpoint of thermodynamics (Vol. II., Chap. III.). In the meantime we may conclude this chapter by a short account of the attempts made to deal with heterogeneous systems containing liquid in contact with saturated vapour, these being characterised by the fact that on compression or rarefaction the volume undergoes considerable change while the pressure remains constant, until in fact one or other of the phases has entirely disappeared. As already pointed out, this horizontal portion of the experimental isothermals (below the critical point) is not taken account of by equations of state, owing to the fact that the actual isothermals are discontinuous whilst the equations refer only to continuous changes.

EMPIRICAL RELATIONS IN CONNECTION WITH SATURATED VAPOURS.

The Ramsay-Young Boiling Point Law.—If we compare two closely related substances A and B, *e.g.* methyl acetate and ethyl acetate, under equal pressures, it will be found that the following relation holds good, namely:—

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B} = \text{a constant}$$

where T_A and T_B are the absolute boiling-points of A and B under a given pressure the same for both, and T'_A and T'_B are also the absolute boiling points under a different pressure, likewise the same for both.

A more accurate expression is—

$$\frac{T'_A}{T'_B} = \frac{T_A}{T_B} + c(T'_A - T_A).$$

This relation was first discovered by Ramsay and Young in 1885 (*Phil. Mag.* [5], **20**, 515, 1885; *ibid.*, **21**, 33; **22**, 37, 1886). In many cases c is practically zero, and the simpler expression holds good. The relation is a valid one from very low pressures up to the critical. Its utility is evident, in that, if the boiling points of a given substance are known over a wide pressure range, and if a few similar determinations be made in the case of a second substance, the remaining values of the boiling points of the second substance may be calculated over the pressure range for which the first substance was measured. The constancy or lack of constancy of c may also be used as a test of normality or abnormality in connection with the molecular state of liquids. For the connection between the Ramsay-Young Boiling Point Law and Bertrand's vapour-pressure formula, the reader is referred to the paper by A. W. Porter (*Phil. Mag.* [6], **13**, p. 724, 1907).

The Vapour Pressure Formulæ of Biot, Rankine, Hertz, Bertrand, and van der Waals.—To describe the variation of the pressure of saturated vapour (in contact with a liquid) with temperature, Biot proposed the following:—

$$\log p = a + b\alpha^t + c\beta^t.$$

Rankine later suggested the expression—

$$\log p = a - \frac{\beta}{T} - \frac{\gamma}{T^2}$$

where p is the vapour pressure, a, β, and γ are empirical constants to be obtained by experiment, and T is the absolute temperature to which p refers. This type of formula is in frequent use, as it reproduces experimental values fairly well. A closer approximation may be obtained, however, by employing the relation due to Bertrand, namely—

$$p = G\left(\frac{T - a}{T}\right)^{n} \text{ or } p^{\frac{1}{n}} = g\left(1 - \frac{a}{T}\right)$$

G, g, a and n being likewise empirical constants.

Recently, however, considerable attention has been drawn chiefly by the work of Nernst and others in connection with the new theorem of heat (Vol. II., Chap. XIII.) to the expression first proposed by Hertz (*Wied. Ann.*, **17**, 199, 1882), *viz.*—

$$\log p \quad k_1 - k_2 \log T - \frac{k_3}{T}.$$

This has been applied, for example, by Knudsen to the case of the vapour pressure of mercury (*Ann. der Physik* [4], **29**, 179, 1909), in connection with his new method of determination of very small [1] vapour pressures. The expression in this case becomes—

$$\log_{10} p = 10{\cdot}5724 - 0{\cdot}847 \log_{10} T - \frac{3342{\cdot}26}{T}$$

The values for the constants chosen by Knudsen reproduce the experimental results particularly well at low temperature, *i.e.* not exceeding 100° C. The same formula has been very thoroughly tested by Smith and Menzies (*Journ. Amer. Chem. Soc.*, **32**, 1434, 1910) who employ it in the form—

$$\log_{10} p = 9{\cdot}9073436 - 0{\cdot}6519904 \log_{10} T - \frac{3276{\cdot}628}{T}.$$

In the two tables on next page are given the results obtained experimentally by various investigators and at the same time the calculated values obtained by the above formula. The measurements of Smith and Menzies extend over the range 250° C. to 435° C. and have been carried out in a particularly accurate manner. Their paper should be consulted as regards the kind and magnitude of the errors which vitiate a large number of determinations of vapour pressure. It is obvious that the above formula may be tested either by calculation of pressure at a given temperature, or inversely by the calculation of the temperature from a given observed pressure. In the first of the two tables (see next page), the pressures are calculated from the temperatures. In the second the temperatures are calculated from the observed pressure values. These tables contain only a selection from the available data. A more complete account is given by Smith and Menzies in the paper referred to.

The chief advantage of the formula is the wide range over which it is fairly accurate.

The empirical vapour-pressure formula of van der Waals may be written in the form—

$$\log \frac{p_c}{p} = f\left(\frac{T_c}{T} - 1\right)$$

---

[1] For a still newer method, depending upon the damping of vibration of a quartz fibre, *cf.* F. Haber, *Zeitsch. Elektrochem.*, **20**, 296, 1914.

VAPOUR PRESSURE OF MERCURY AT VARIOUS TEMPERATURES BELOW 200° C.

Temperature Observed, °C.	Pressure Observed in mm. of Mercury.	Observer.	Pressure Calculated by Smith and Menzies.
0	0·0001846	Knudsen	0·000207
7·1	0·0003667	,,	0·000409
16	0·0010	Morley	0·000922
30	0·0027	,,	0·00298
50	0·0113	,,	0·01339
70	0·0404	,,	0·0529
89·4	0·16	Hertz	0·1575
117	0·71	,,	0·6552
154·2	3·49	,,	3·328
165·8	5·52	,,	5·216
177·4	8·20	,,	7·985
190·4	12·89	,,	12·54

VAPOUR PRESSURE OF MERCURY AT VARIOUS TEMPERATURES BETWEEN 200° C. AND 880° C.

Pressure Observed in mm.	Observer.	Temperature Observed.	Temperature Calculated by Smith and Menzies.
20·35	Hertz	203·0	205·29
51·85	Young	236·9	236·78
82·08	Smith and Menzies	253·97	253·91
128·57	,,	271·82	271·81
210·79	,,	293·07	293·04
309·73	,,	310·75	310·77
498·01	,,	334·16	334·30
732·13	,,	354·85	354·87
765·44	,,	357·32	357·34
1210·58	,,	383·95	383·99
1847·35	,,	410·66	410·69
2125·78	,,	420·10	420·07
2624·35	,,	434·71	434·65
3230	Cailletet, Colardeau, and Rivière	450	449·65
6080	,,	500	499·7
10488	,,	550	549·0
16948	,,	600	599·4
38000	,,	700	696·3
77520	,,	800	804·6
123120	,,	880	889·6

in which p is the vapour-pressure corresponding to the temperature T, and f is regarded as a universal constant.

The following values of f were calculated from data obtained with carbon dioxide :—

Temperature centigrade.	*f*.
+ 20	2·90
± 0	2·85
− 10	2·85
− 30	2·84
− 50	2·86
− 60	2·87
− 63·13	2·88

It will be observed that *f* is very nearly constant over this range of temperature. The following values of *f* were obtained in the case of a few typical substances:—

"Normal" Substances (Molecules Unpolymerised).

Substance.	*f*.	Substance.	*f*.
Hydrogen	2·10	Benzene	2·89
Nitrogen	2·27	Argon[1]	(2·18) 2·25
Oxygen	2·50	Krypton	(2·30) 2·39
Carbon dioxide	2·86	Xenon	(2·34) 2·38
Ether	3·01		

"Abnormal" Substances (Molecules Polymerised in Liquid State).

Substance.	*f*.
Water	3·26
Acetic acid	3·48
Methyl alcohol	3·75
Ethyl alcohol	3·91

The monatomic substances (Ar, Kr, Xe) appear to belong to a group by themselves. The value of *f* is not quite independent of the chemical nature of the substance under examination, this being especially so in the case of polymerised substances.

The pressure of saturated vapour depends only on the temperature, being independent of the volume of either phase as long as the volume of either phase is great compared with molecular dimensions.

Now the above vapour-pressure formula may be written in the "reduced" form thus—

$$\log p_r = f\left(1 - \frac{1}{T_r}\right),$$

---

[1] More recently, Onnes (*Proc. Roy. Soc. Amsterdam*, 13, 1019) finds that *f* for Argon increases from 2·415 (at − 140·8° C. and pressure 22·185 atmospheres) to 2·577 (at + 125·49° C. and 42·457 atmospheres), but there is no regularity in the variation.

and since the temperature fixes the pressure it follows from the principle of corresponding states that two bodies at corresponding temperatures, *i.e.* possessing the same value for T_r, must likewise be at corresponding pressures, *i.e.* possess the same value for p_r. Hence, even if f is not a universal constant and not even independent of temperature, it follows that it must have the same numerical value for substances in corresponding states.

MOLECULAR ASSOCIATION OR POLYMERISATION IN PURE LIQUIDS.

So far we have endeavoured to investigate the behaviour of liquids and gases from the purely physical standpoint, *i.e.* from the standpoint of distribution of molecules in space. The exceptions and discrepancies which arise, however, in this method of treatment seem only to have an explanation if we take into account the possibility of "chemical" effects such as polymerisation or of dissociation of molecules themselves. The first point which arises is the question of the molecular weight of liquids actually *in the liquid state*. The usual methods of determining the molecular weight of a volatile substance are based upon determinations of vapour density, *e.g.* the methods of Dumas, Hoffmann or Victor Meyer (see Young's *Stoichiometry* for details). It is obvious, however, that the result one obtains by such means is the molecular weight of the body in the state of vapour. In water, for example, the result is 18, for ethyl alcohol 46, for benzene 78. Fortunately, there are one or two methods available which show the existence of polymerisation of molecules of certain liquids at least qualitatively. None of the methods is particularly sound, but the one most frequently employed is that known as the *Eotvos Ramsay-Shields* method. It depends on a relationship first deduced by Eötvös in 1885 and applied as a practical method by Ramsay and Shields in 1893. Eötvös showed (*Annalen der Physik*, **27**, 448, 1885) from general considerations based upon the conception of corresponding states that the expression $\frac{d}{dt}\{\gamma(Mv)^{\frac{2}{3}}\}$, that is the temperature coefficient of the "molecular surface energy" (γ being surface tension, v the specific volume of the liquid, and M the molecular weight of the liquid as liquid), which could be represented by a curve of some kind obtained by plotting temperature against "molecular surface energy," $(Mv)^{\frac{2}{3}}$, should be the same type of curve for all substances. Having carried out some determinations with ether, he found experimentally that the curve was a straight line approximately, and hence the above expression $\frac{d}{dt}\{\gamma(Mv)^{\frac{2}{3}}\}$ was a constant. Eötvös wrote his relation in the form $\gamma(Mv)^{\frac{2}{3}} = k(T - T_0)$, where T_0 is a temperature not very different from the critical, k having the value 2·27. Note that Eötvös did not show theoretically that the expression should be a constant. What he did was to show that whatever shape the curve might be for one substance it would be the same for all others.

The experimental work of Ramsay and Shields (see Young's *Stoi-*

chiometry), however, while supporting Eötvös's generalisation in many cases, such as benzene, carbon disulphide, and series of esters, resulted in the discovery of marked discrepancies, notably in the cases of water, acetic and fatty acids in general, and the alcohols. These substances did not give the constant $-2\cdot1$ (Ramsay and Shields' value of k), but gave a much smaller number. In working out these calculations the ordinary molecular weight, *i.e.* the molecular weight as given by *vapour density* determinations, was employed. Assuming the correctness of the Eötvös theoretical generalisation,[1] the most reasonable explanation of the anomalies which suggested itself was to consider the molecular weight of the "abnormal" substances as *differing* in the liquid and in the vapour states. As a matter of fact, in order to obtain the constant $-2\cdot1$ it was necessary to ascribe a higher molecular weight to these substances in the liquid state than in the state of vapour. That is, a fraction of the molecules of these abnormal substances in the liquid state was regarded as associated or polymerised. The method of using the Eötvös formula for the calculation of M consists in writing it in the approximate form—

$$\frac{\gamma_0(Mv_0)^{\frac{2}{3}} - \gamma_1(Mv_1)^{\frac{2}{3}}}{t_0 - t_1} = -2\cdot1$$

where γ_0 and v_0 refer to the temperature t_0, and γ_1, v_1 to the temperature t_1. Note that M is considered to be constant between t_0 and t_1 (an approximation). The expression for M is therefore—

$$M = \left\{\frac{-2\cdot1(t_0 - t_1)}{\gamma_0 v_0^{\frac{2}{3}} - \gamma_1 v_1^{\frac{2}{3}}}\right\}^{\frac{3}{2}}.$$

For the experimental details of the determination of the surface tension, etc., reference must be made to the original paper (*Trans. Chem. Soc.*, **63**, 1089, 1893).

Besides observing that the constant obtained differed from $-2\cdot1$, in these associated liquids it was likewise found that its value varied with the temperature, showing that the degree of dissociation varied with the temperature, tending towards unity, *i.e.* the normal molecular state, as the temperature rose. If we denote "degree of association" by n, *i.e.* the number of times the molecular weight is greater than its value in the state of vapour, we find the following:—

Water.		Acetic Acid.		Methyl Alcohol.		Ethyl Alcohol.	
t° C.	n	t° C.	n	t° C.	n	t° C.	n
0	1·71	20	2·13	− 90	2·65	− 90	2·03
20	1·64	60	1·99	+ 20	2·32	+ 20	1·65
60	1·52	100	1·86	110	2·06	100	1·39
100	1·40	140	1·72	180	1·86	180	1·15
140	1·29	280	1·30	220	1·75	220	1·03

---

[1] Eötvös's reasoning cannot be regarded as very rigid. See a paper by van der Waals, *Zeitsch. physik. Chem.*, **13**, 713, 1894.

For a general discussion regarding the constitution of water, from which it seems fairly certain that ice consists mainly of trihydrol $(H_2O)_3$, together with a little dihydrol $(H_2O)_2$, and still less monhydrol, H_2O—liquid water at ordinary temperatures being mainly dihydrol with some trihydrol and some monhydrol, the latter increasing as temperature rises, the vapour being practically monhydrol—the reader is referred to the *Trans. Faraday Soc.*, **6**, Part I., p. 71, 1910. It may be noted in passing that it is precisely those liquids which are themselves associated which, when acting as solvents, have the most marked property of causing dissociation, *i.e.* electrolytic dissociation, of many solutes such as acids, bases, and salts.

It should be noted that the form of the Eötvös expression actually employed by Ramsay and Shields was somewhat different from that of the original, an empirical term d being introduced and the expression written thus:—

$$\gamma(\mathrm{M}v)^{\frac{2}{3}} = k(\tau \quad - \tau - d)$$

where τ_c is the critical temperature, τ the temperature of measurement, and d has usually the numerical value 6. The k in this expression, as used by Ramsay and Shields, has the value 2·12.

Recent investigation and discussion has, however, thrown some doubt on the numerical values of the degree of polymerisation obtained by the above means, some authors considering that the estimates of Ramsay and Shields are too high, others that polymerisation is a much more general phenomenon and that possibly even normal liquids are not quite free from it.

A recent advance in connection with the relation of surface energy to molecular complexity is due to Bennett (*Zeitsch. physikal. Chem.*, **48**, 475, 1913, and *Trans. Chem. Soc.*, **107**, 351, 1915), who makes use of the total molecular surface energy in place of the free molecular surface energy already employed in the preceding paragraphs. The distinction between these two terms rests on an application of the Gibbs-Helmholtz thermodynamical equation (compare Vol. II., Chap. I.). In the case of acetic acid it is shown that the free molecular surface energy falls slightly as the temperature rises whilst the total molecular surface energy remains practically constant. The constancy of the latter term indicates normal behaviour. The conclusion is therefore drawn that between 15° and 150° C. acetic acid consists almost entirely of the polymerised form $(CH_3COOH)_2$.

The whole problem of molecular complexity is only partially solved at the present time. A very complete account of the subject is given by W. E. S. Turner in *Molecular Association* (Monographs on Inorganic and Physical Chemistry (Longmans)).

THE SOLID STATE OF MATTER.

CRYSTAL STRUCTURE AND ITS ELUCIDATION BY MEANS OF X-RAYS.

We are already familiar with the fact that the true solid state is characterised by the existence of crystalline form. Amorphous solids, such as glass, are grouped as liquids of high viscosity. A true solid separates from solution or from vapour in the form of crystals having definite properties, the melting point, for example. Amorphous solids, *i.e.* supercooled liquids, possess no definite melting point. Crystalline form exhibits many varieties into the details of which it is quite impossible to enter in this place. The classification of crystalline forms is based on three main considerations: (1) constancy of corresponding interfacial angles on all crystals of one and the same substance; (2) the existence of simple numerical relations between the co-ordinates of all planes which are possible on crystals of the same substance; (3) the fact of symmetry. Symmetry is determined with respect to certain planes called planes of symmetry. A plane of symmetry is an imaginary plane dividing a crystal into two parts, each of which is the mirror image of the other. According to the number of such planes which can actually be drawn in different directions through crystals the latter have been divided into seven systems. This classification also involves certain facts about the axes, *i.e.* the crystallographic axes or space co-ordinates in terms of which the geometrical form of the crystal can be described. The seven systems are the regular or cubic system; the hexagonal system; the quadratic or tetragonal system; the rhombic system; the trigonal system; the monosymmetric or monoclinic system; the asymmetric or triclinic system. Each of these systems is further subdivided into classes of which there are thirty-two in all. For information regarding these systems and classes a textbook of crystallography must be consulted.[1]

For our present purpose it will suffice to restrict ourselves to one or two examples of the simplest type of crystalline form, namely, the cubic system, and to indicate how the recent general method of investigation by means of X-rays developed by W. H. and W. L. Bragg[2] may be employed to elucidate the structure of crystals, by applying the method to a few simple cases.

Crystals belonging to the regular or cubic system are built up on three equal axes at right angles to one another. The crystal possesses in all nine planes of symmetry, namely, three principal planes at right angles, and six secondary planes which are inclined at 60° to one another. This system represents the highest order of symmetry. Among well-known substances which belong to this system we may mention anhydrous chlorides of the alkali metals, the diamond and zinc blende, ZnS.

---

[1] For example, Tutton's *Crystallography and Practical Crystal Measurement*, or the forthcoming work by T. V. Barker on Crystallography in this series of textbooks.

[2] *X-Rays and Crystal Structure*, by W. H. and W. L. Bragg. Also W. H. Bragg, *Trans. Chem. Soc.*, 109, 260, 1916.

It is important to observe that the mere external form or habit which a crystal exhibits is not the fundamental factor in its characterisation. A crystal has to be examined and finally classified according to the relative lengths of its axes, their inclination to one another, and the values of the interfacial angles. Numerous forms externally different can thus be ascribed to the same system.

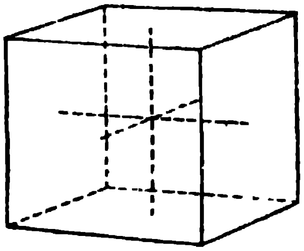


Fig. 21. (From P. H. Williams' *Elements of Crystallography*, H. Holt & Co.)

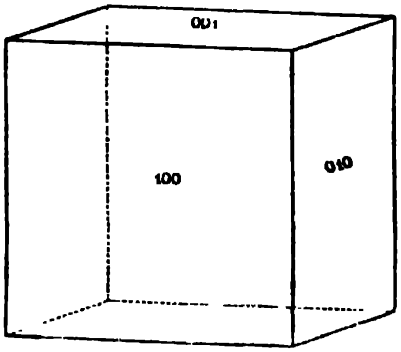


Fig. 22.—The Cube. (From Tutton's *Crystallography*, Macmillan.)

As regards the cubic system, several types of crystals are known, the most important of which are illustrated in the Figs. 22 to 25. What they have in common are three rectangular axes of equal length as shown by the dotted lines in Fig. 21. The forms referred to are: the cube, the regular octahedron, the regular dodecahedron, and the regular tetrahedron.

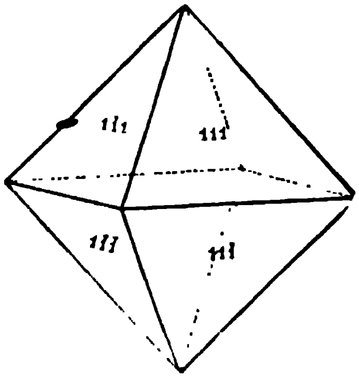


Fig. 23.—The Octahedron. (From Tutton's *Crystallography*, Macmillan.)

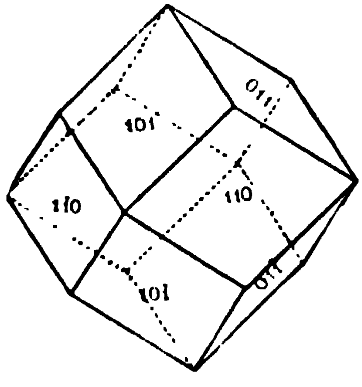


Fig. 24.—The Rhombic Dodecahedron, (From Tutton's *Crystallography*. Macmillan.)

As actual examples one may cite common salt, which crystallises in cubes, alum which crystallises in regular octahedra, and the garnet which frequently crystallises in regular dodecahedra. The particular form which manifests itself depends to a large extent upon the conditions under which crystallisation takes place. The numbering of the faces will be considered later. (It may be noted that the numbering refers to faces *nearest* the observer, not to the faces indicated by dotted lines.)

Each of the above forms is not equally simple. All can be regarded as a matter of fact as formed from the regular octahedron. Fig. 26 indicates the relation of the regular tetrahedron to the regular octahedron, the axes being the same for both.

It was early recognised that the external symmetry exhibited by crystals is the outward and visible sign of an internal regularity of arrangement of the ultimate particles of matter which compose the crystal. What these ultimate particles are has recently been demonstrated as a result of investigation by means of the X-ray spectrometer. It is now known that the essential unit of matter is the atom itself, atoms being arranged in definite parallel planes separated from one another by distances of the order 10^{-8} cm. In some cases these planes are all similarly constituted—either containing atoms all of the same kind as in elements, or containing, in the case of compounds, more than one kind of atom—or the planes may consist alternately of the same atoms. Our present knowledge of the composition of successive planes, and their distances apart, represents one of the chief results attained by the study of crystals by means of X-rays.

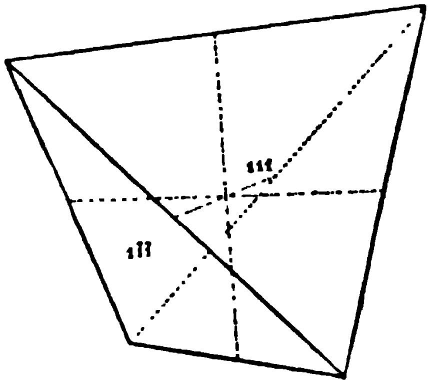


FIG. 25.—The Tetrahedron. (From Tutton's *Crystallography*, Macmillan.)

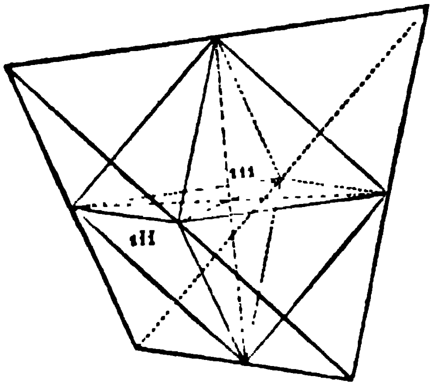


FIG. 26.—Relation of Tetrahedron to Octahedron. (From Tutton's *Crystallography*, Macmillan.)

The existence of planes in various directions in a crystal, parallel to the sides of the crystal are indicated diagrammatically in Fig. 27.

These planes have a real existence in that they are atom-bearing planes. We shall have occasion to refer to these planes later, when considering the part they play in reflecting a beam of X-rays.

Howsoever complicated a crystal may be, as regards its chemical composition, it is always possible to construct a representative space model known as the space lattice in which a single point is used to mark the centre of gravity of each chemical group or unit. The resulting figure consists of a series of points in space which represent the structure upon which the crystal is based. This idea of the space lattice developed though not originated by Bravais, is of great importance in the systematisation of geometrical forms, and it is much simpler to deal, not with the crystal itself, but with the space lattice corresponding to it.

Restricting ourselves to the cubic or regular system, we have now to consider in more detail the relations of several of the planes to one another, or what is the same thing, we have to consider the faces parallel to these planes, for crystal faces represent the possible ways of arranging points of the space lattice in planes. We shall consider three different kinds of planes, differing in respect of their position with reference to the rectangular axes of the cube. Three such planes are indicated in Fig. 28, namely, the face GEAF, the face CEFB, and the face ABC.

The axes of the space lattice representing the crystal are parallel to OY, OX, and OZ, the origin being O. We have now to locate the face GEAF. Along the OX axis the face is placed at a perfectly definite position cutting off the intercept OA. The face is at the same time parallel to the Y and Z axes. When a face is parallel to an axis its intercept on that axis is infinite. That is, referring the face GEAF to the three axes in the order named (*viz.* OY, OX, and OZ), we would say that the intercepts are to one another in the ratio ∞ : OA : ∞.

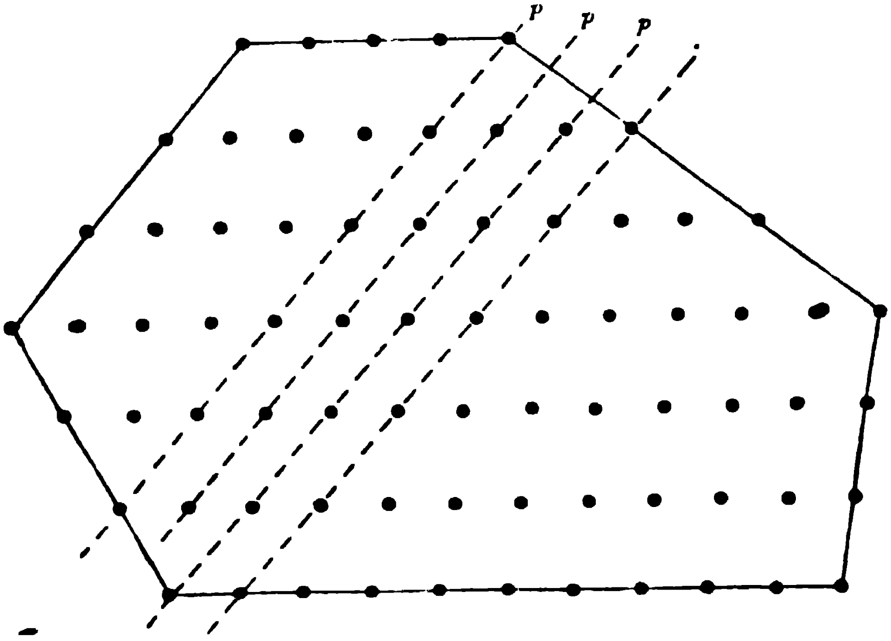


FIG. 27. (From Bragg's *X-Rays and Crystal Structure*, G. Bell & Sons.)

It is convenient to express intercepts in terms of the smallest whole numbers, the unit of length being the side of the fundamental cubic lattice.[1] That is, we write unity in place of the finite distance OA and express the face GEAF as ∞ : 1 : ∞. The reciprocal of the intercepts as thus expressed are known as the *indices* of the face, and it is usual in crystallography to locate faces in terms of indices. The indices of the face GEAF are obviously 0 : 1 : 0. The locating of the remaining tive faces of the cube follows the same method. For example, the face DGFB possesses intercepts OB : ∞ : ∞, always taking the axes in the order OY, OX, OZ. The indices of this face are therefore 1 : 0 : 0, and this face is known as the (100) face. This explains the numbering of the faces of the cube (Fig. 22).

---

[1] This point is discussed *inter alia* by Bragg, *X-Rays and Crystal Structure*, p. 53 *seq.*

The next plane to be considered is that represented by CEFB. The intercept along OY is the finite distance OB, the intercept along OX is infinite for the plane is parallel to OX, the intercept along OZ being OC, where OC = OB. The intercepts are therefore OB : ∞ : OC, which becomes 1 : ∞ : 1, and therefore the indices are 1 : 0 : 1, the face being designated as the (101) face. Another plane quite similar to the CEFB plane is that denoted by CGFO (not shown in Fig. 28). This plane has intercepts OB : OA : ∞, or 1 : 1 : ∞, the indices being 1 : 1 : 0, the face itself being the (110) face. The third type of face or plane is that represented by the area ABC. This face is not parallel to any of the axes. Instead it cuts off equal intercepts, *viz.* OB, OA, and OC. The indices are therefore 1 : 1 : 1, and the symbol (111) indicates the face itself. This face appears in octahedra (Fig. 23). If the face lies to the left of, or below the origin of axes, then one or more of the indices has a negative sign placed above it to indicate with greater precision the actual position of the face.

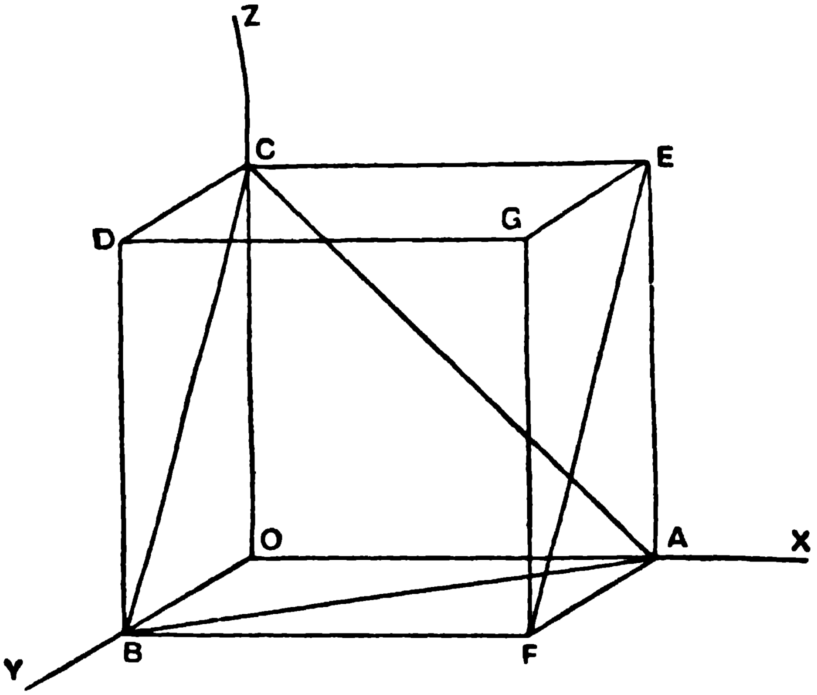
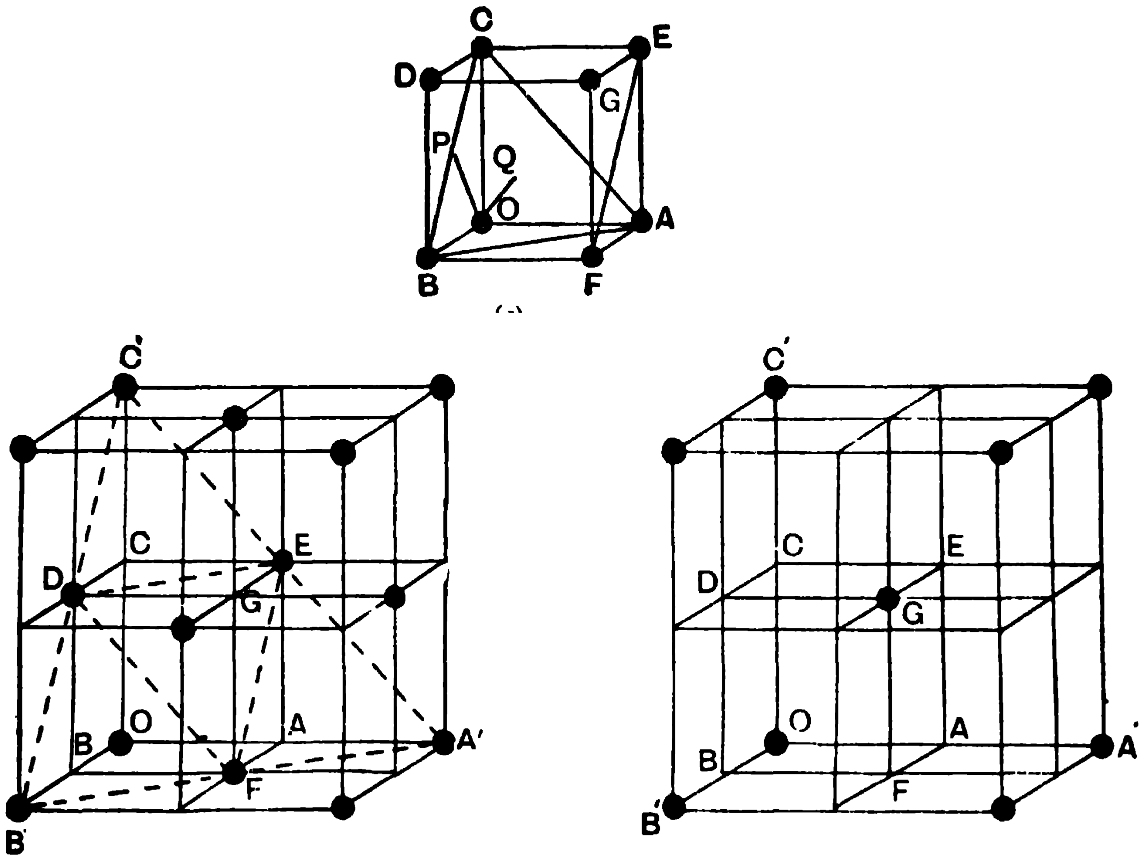


FIG. 28. (From Bragg's *X-Rays and Crystal Structure*, G. Bell & Sons.)

In regard to the three faces (100), (110), and (111), which we have been considering it is important to bear in mind that we are only concerned with those which really exist, *i.e.* those which have certain points of the space lattice lying in them. An actual crystal is built up of a great number of elementary space lattices; consequently we find repetition of the same kind of plane, identical planes being parallel to one another and lying at a fixed distance apart. We can imagine the process of slicing down a crystal, taking plane after plane, and the first point which arises is the relative spacing of the three types of plane represented by (100), (110), and (111) respectively.

Let us consider the simplest type of lattice unit, belonging to the cubic system, namely, a cube with a point—or if we like, an atom in the actual case—at each corner (Fig. 29*a*). The length OB is the distance, which we shall denote by *d*, between two parallel (100) faces. The distance apart of the (101) faces, such as CEFB, is OP. This is likewise the distance apart of every (110) face, such as the unmarked one CGFO, since a (101) face is identical with a (110) face as far as distance apart is concerned. The distance apart of the (111) faces is OQ where OQ is the perpendicular from O on the face ABC. It then follows as a geometrical necessity that—



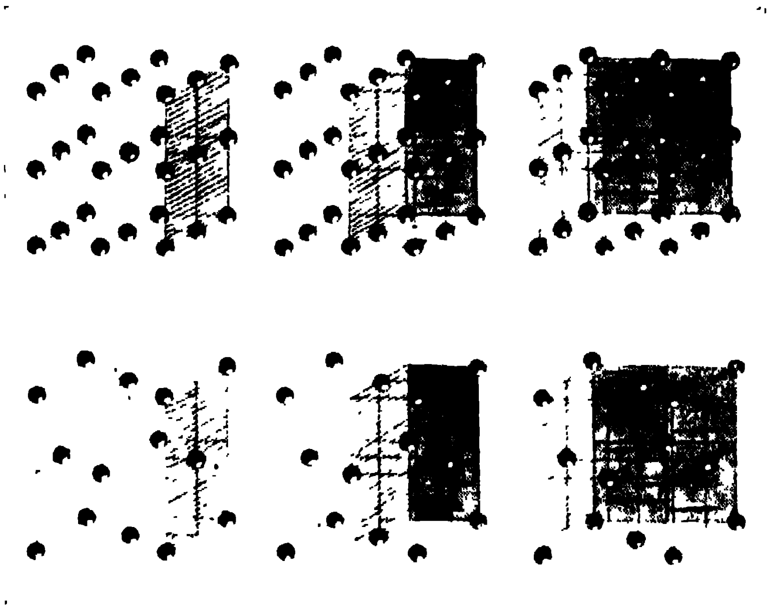
(*a*)

(*b*) (*c*)

FIG. 29. (From Bragg's *X-Rays and Crystal Structure*, G. Bell & Sons.)

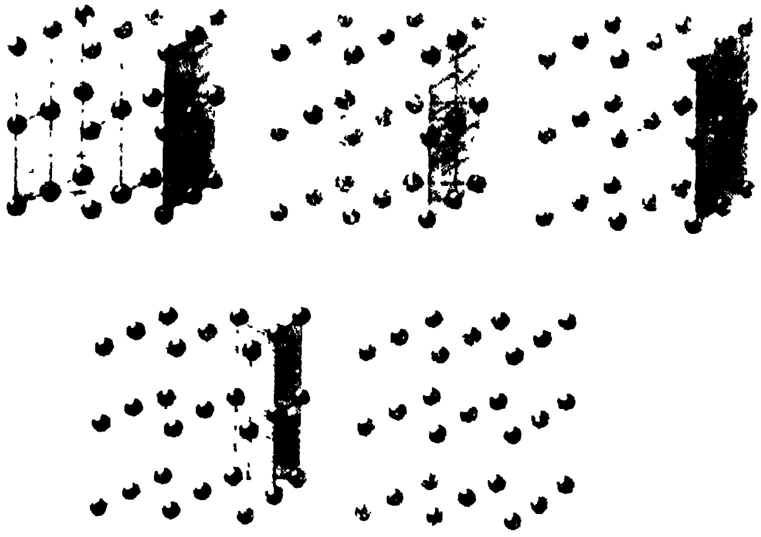
$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} \qquad 1 : \sqrt{2} : \sqrt{3}.$$

But the simple cube, with points at the eight corners, is not the only kind of cubic lattice. It is known that two others, called respectively, the *face-centred* cubic lattice (Fig. 29*b*), and the *cube-centred* lattice (Fig. 29*c*) are possible. Each of these unit lattices is twice the



(*a*)

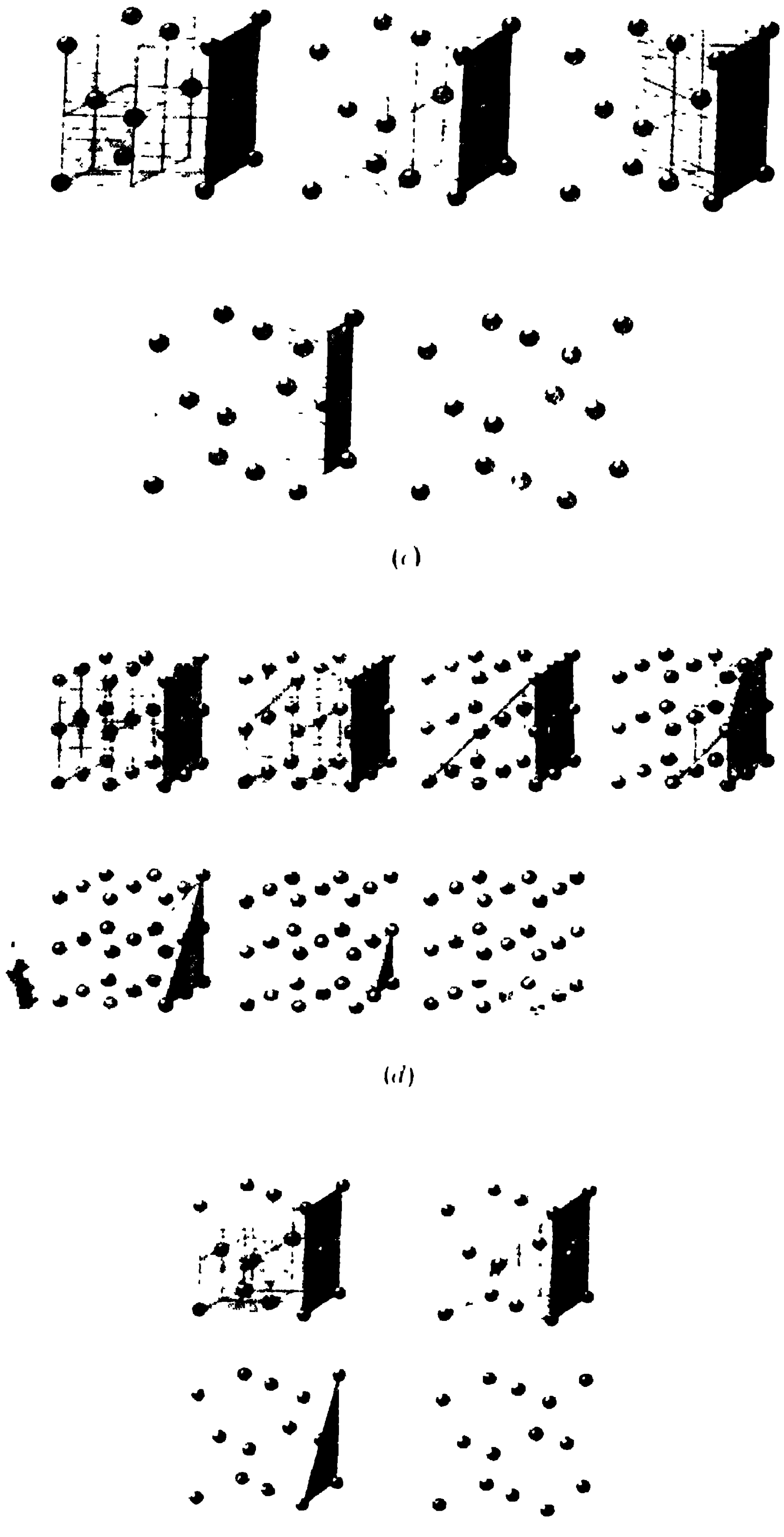
Two arrangements, the upper a simple cubic, the lower a face-centred cubic, which have the same spacings for the planes parallel to a cube face (100).



(*b*)

This and the next figure show that the (110) planes also have the same spacing in the two arrangements. It is $1/\sqrt{2}$ of the (100) spacing.

FIG. 30. (After Bragg, *Chemical Society Transactions*, 1916.)



(c)

(d)

(e)

Comparison of figs. *d* and *e* shows that the (111) spacing for the face-centred arrangement is twice as great as for the simple cubic.

FIG. 30. (After Bragg, *Chemical Society Transactions*, 1916.)

size of the simple cube, *i.e.* the length of each side is double that of Fig. 29*a*. A crystal may be built up on either of these structures in preference to the simple "corner" cube structure. The Figs. 29*b* and *c* indicate clearly the face-centred arrangement and the cube-centred arrangement respectively. The reason why these are drawn on twice the scale of *a* is simply this. Let us suppose all the possible corners[1] filled up with lattice points—each representing an atom—then the smallest unit should be identical in dimensions with Fig. 29*a*. This is only possible if the face-centred and cube-centred *units* themselves are on double the scale of the *simple* cube unit. In fact if this "filling in" were done, Figs. *b* and *c* would represent a collection of eight actual units of the simple cube type.

We have now to find out the relative distances apart of the (100), (110), and (111) faces in the case of a crystal built up on the face-centred lattice and on the cube-centred lattice respectively. Particular attention is to be paid to the face-centred arrangement as this is the one met with most frequently in actual practice. We shall consider the face-centred lattice (Fig. 29*b*) first.

It will be seen that successive (100) planes lie just as far apart as they do in Fig. 29*a*. That is, *d* (100) is the same as before. The same thing is true of the (110) faces, *d* (110) being the same as before. In the case of the (111) faces, however, the distance *d* (111) is double that of the simple corner cube arrangement. It is essential to consider only those planes which actually are point or atom bearing. Fig. 29*b* has a (111) plane passing through O, embracing points on contiguous lattices, then one passing through DEF, *i.e.* the plane A′B′C′, the plane ABC being missing (in that there are no points or atoms upon it). The distance *d* (111) is the perpendicular from O on A′B′C′. In the case of the face-centred lattice we must therefore write—

$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2}.$$

These conclusions will be rendered clearer by means of the accompanying plate (Fig. 30), in which the various planes are shown, the lattice being imagined to be sliced in stages so as to show the atom-bearing planes one after the other until all are accounted for.

It is to be observed that in Fig. 30(*a*) the lattices shown in the upper row contain eight actual units of the simple cube type. The same is true of Fig. 30(*b*) and (*d*). On the other hand the actual lattice shown in the lower row of (*a*) and all in (*c*) and (*e*) represent the face-centred unit itself. Further, the actual (110) planes shown in Fig. 30(*b*) and (*c*) correspond in position with, *i.e.* are parallel to, the (110) planes referred to in Fig. 28 as CGFO.

Turning now to Fig. 29*c*, which shows a single unit of the cube-centred type, it is clear that *d* (100) and *d* (111) are the same as for the simple cube lattice Fig. 29*a*, but *d* (110) is twice as great as before. Hence for the cube-centred lattice we have—

---

[1] **A corner, in this sense, denotes the position where four lines meet.**

$$\frac{1}{d_{(100)}} : \frac{1}{d_{(110)}} : \frac{1}{d_{(111)}} = 1 : \frac{1}{2} : \sqrt{3}.$$

Having indicated very briefly the various kinds of planes and types of lattice unit upon which a cubic crystal may be built up, we must now turn to the question of how the spacing of planes in actual crystals has been determined by means of the X-ray spectrometer; for it is obvious from what has been said that a knowledge of such spacing will give us information regarding the nature of the lattice upon which the crystal is based. The X-ray method is also capable of telling us what the chemical composition of the various planes is, and, in short, the mode of distribution of the various atoms composing the crystal.

X-rays are now known to be light of extremely short wave-length, and the idea that such short waves might be capable of determining the structure of a crystal was first suggested by Laue in 1912 (*Sitz. K. Bay. Akad.*, June, 1912), who passed a beam of X-rays through a crystal and examined the diffraction spectra obtained. The results, though fully substantiating the general correctness of Laue's suggestion, were by no means easy to interpret. The advance made by the Braggs is due to the suggestion of W. L. Bragg, namely, to use the crystal as a *reflection* grating, the resulting spectra being much simpler and more amenable to theoretical treatment. Before giving an outline of this method it is necessary to explain what is meant by a reflection grating in the case of ordinary light.

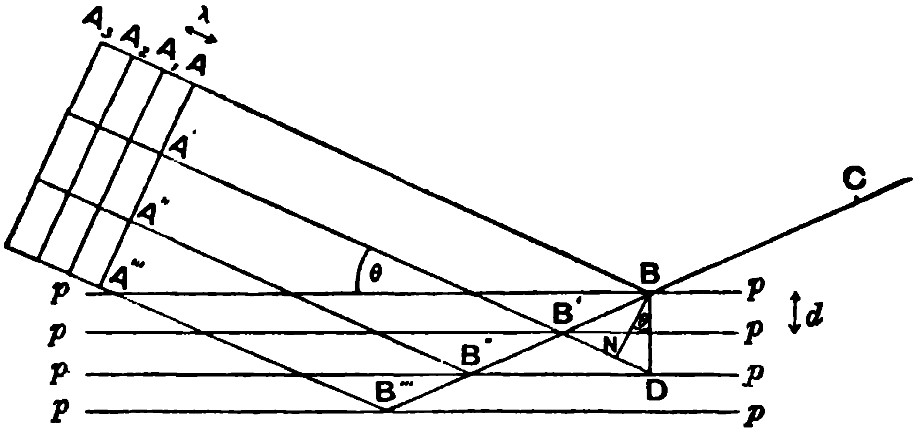


FIG. 31. (After Bragg.)

Let us suppose that we have a number of glass plates lying on one another, with reflecting surfaces indicated by the horizontal lines *pppp* (Fig. 31), and further suppose that AA'A''A''' denotes an advancing train of light waves, the light being monochromatic, of wave-length λ.

Consider those waves which after reflection all move in the direction BC. It is obvious that some of the waves travel a different route from others, though they may all start from the position AA''' and end at C, the routes being ABC, A'B'C, A''B''C, and so on. Let us compare the two routes ABC and A'B'C. It is easily seen that the route A'B'C is longer than the route ABC by the amount ND, which is equal to $2d \sin \theta$, where d is the distance between the horizontal faces or the spacing of the planes, and θ is the glancing angle. The vibrations in the wave-front AA‴ are all in the same phase, but since they do not follow the same path they will not necessarily be in the same phase on arriving at C. They will only be in the same phase when the path difference $2d \sin \theta$ is one wave-length, or an integral multiple of one wave-length. When these conditions are realised the waves at C will reinforce one another and a bright band or spot is produced at C. That is, it is only when the angle θ has certain values that a reflection will be observable through a spectrometer eyepiece placed at C. These values are given by—

$$\begin{aligned} \lambda &= 2d \sin \theta_1, \\ 2\lambda &= 2d \sin \theta_2 \\ \\ n\lambda &= 2d \sin \theta_n. \end{aligned}$$

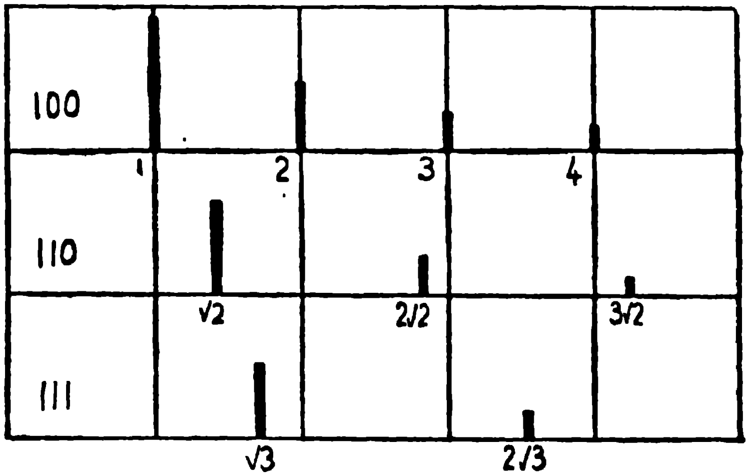
The reflection at the angle θ_1 is called the reflection of the first order, that at θ_2 the second order, and so on. If the difference in the path is not an even multiple of λ, the waves arriving at C will tend to destroy one another, and if there be many reflecting planes this destruction will be complete. The special positions of brightness obtained when the waves reinforce each other can be regarded as the spectra of the incident light. The value of θ can be altered to θ_1, θ_2, etc., by turning the pile of plates on an axis.

It is evident that the *relative* magnitude of the spacing d and of the wave-length λ is of the greatest importance. If d were extremely small compared with λ, no value of θ could be found which would satisfy the relation $n\lambda = 2d \sin \theta$, for $\sin \theta$ cannot be greater than unity. That is, no reflection could be obtained in such a case. In actual practice, a reflection grating is used instead of a pile of plates, and, if sodium light be employed ($\lambda = 0{\cdot}0000589$ cm.), a suitable value for the spacing of the lines ruled on the grating is $d = 0{\cdot}000143$ cm., *i.e.* the two quantities must be of the same order of magnitude.

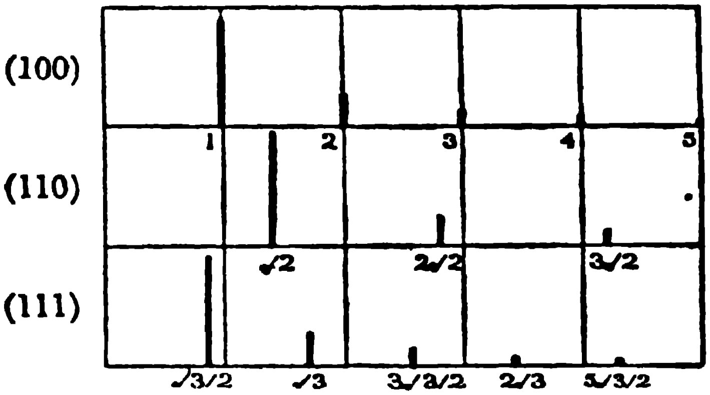
Now it is known, on the basis of considerations dealing with the size of molecules and atoms (Chap. I.), that the average distance of atoms apart in solids is of the order 10^{-8} cm. A spacing of this order would be quite without effect on ordinary light or even on ultra-violet light, but reflection effects could be produced with a light whose wave-length is of the order 10^{-8} cm. It is known on other grounds that this is a very probable value for the wave-lengths of X-rays, and the work with the X-ray spectrometer has shown that reflections of X-rays, in agreement with the above relations, regarding difference of path, can actually be obtained. In place of the pile of plates we simply have a crystal, the internal atomic layers of which function as the reflecting surfaces. As a means of detecting the various positions of reflection maxima an ionisation chamber filled with an easily ionised gas, such as SO_2 or methyl bromide, is employed, the chamber being connected to an electroscope and the ionisation measured in the ordinary way. The ionisation chamber is mounted on an arm which takes the place of the telescope in the ordinary spectrometer and the crystal upon which the X-rays impinge can be rotated. At those glancing angles at which reflection takes place, the reflected beam passes through an aluminium window into the ionisation chamber, causing ionisation indirectly, and the fact of reflection is thus observed by means of the electroscope. By rotating the crystal one can obtain the reflections—reflection spectra—of various orders, and, knowing θ, the expression $n\lambda = 2d \sin \theta$ allows us to calculate d in terms of λ, or *vice versâ*. Measurements of this nature may be employed to determine whether a given beam of X-rays is homogeneous or not, that is, whether it consists of a single wave-length or of several wave-lengths. Into this problem connected with the nature of the waves themselves we have not space to go. For our present purpose we deal with a homogeneous beam impinging on the surface of a crystal, thereby giving rise to spectra which differ according to the nature of the face, *i.e.* whether it is a (100), a (110), or a (111) face, for as we have seen the spacing d varies in these cases, and consequently the relative positions of the spectra (reflections), as given by the general relation $n\lambda = 2d \sin \theta$, differ also. The first reflection or spectrum is defined as we have seen by the relation $\lambda = 2d \sin \theta$, the second by $2\lambda = 2d \sin \theta_2$, and so on. Further, in the case of ordinary light, when the spectra are normal in behaviour, it is well known that the intensity of successive spectra obtained at the angles θ_1, θ_2, etc., falls off quite regularly. It is thus possible to make beforehand a diagrammatic representation of the kind of spectra which we would expect from each of the three faces, (100), (110), (111), of a crystal which is built on the simple cube form. Fig. 32*a* represents the relative spacing of the reflection lines in this, the simplest case. The ordinates denote intensity of reflected beam, and the abscissæ the values of the angle of setting of the ionisation chamber. The successive positions of the chamber with respect to the crystal, when reflection occurs ought to be in the ratio of the numbers which we have already obtained for the relative spacings of the atom-bearing planes, in directions parallel to the three kinds of faces. Indicating by unity the position of the first spectrum obtained from the (100) face layers, the position of all the others may be calculated. For each face the wave-length and the spacing of the crystal layers parallel to the face examined are connected by the equation $n\lambda = 2d \sin \theta$. Proceeding in exactly the same way in the case of a crystal, which is built up on the face-centred lattice, we obtain the relative positions and intensities of the spectra indicated in Fig. 32*b*.

On examining Fig. 32 *a* and *b* it will be observed that the (100) and (110) faces give exactly the same spectra in each case. That is, if we restricted ourselves to these two faces alone, it would be impossible to distinguish the simple cube lattice from the face-centred lattice. On the other hand, a clear distinction manifests itself when we compare the spectra of the (111) face in the two cases.

We turn now to a set of measurements of an actual crystal of a simple substance, belonging to the regular system, namely, sodium chloride, with the object of determining whether the X-ray spectra obtained are capable of telling us the nature of the lattice upon which the NaCl crystal is built up. A diagrammatic view of the actual positions of these spectra is given in Fig. 33. On examining this diagram we see that the position of the spectra obtained from the layers parallel to the (111) face undoubtedly leads us to attribute a face-centred structure to the NaCl lattice. At the same time we observe certain abnormalities as regards the relative intensities of the successive spectra obtained from this, the (111) face. The intensities of the spectra from the other two faces fall off quite regularly as theory requires. In the case of the (111) face, however, the first order spectrum is abnormally weak, the second abnormally strong, the third abnormally weak, and the fourth abnormally strong. As a matter of fact, if we judged by the strong reflections alone we would attribute a simple cube lattice structure to the substance, but this would be, of course, an unjustifiable proceeding. It is clear that we are dealing with a face-centred arrangement, but there is something



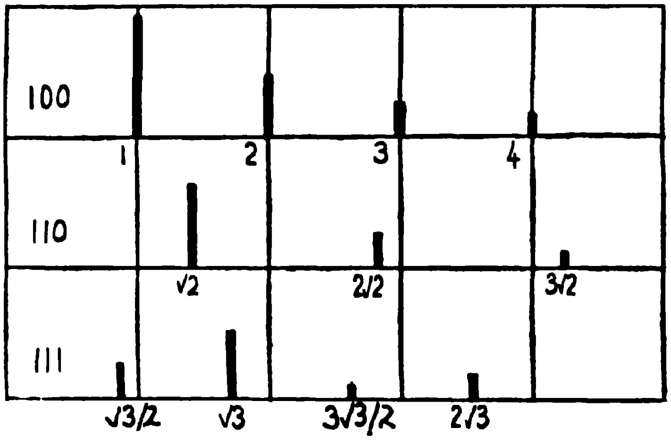
(*a*) Diagram of Spectra of Simple Cube.



(*b*) Diagram of Spectra of Face-centred Cube.

FIG. 32. (After Bragg, *Chemical Society Transactions*, 1916.)

operating which *alternately* enhances and diminishes the intensity of the successive spectra. It is this alternation in the effect which suggested to W. H. and W. L. Bragg the real explanation, and at the same time permitted them to take the most important step in establishing the ***nature*** of the actual reflecting particles themselves. To follow the explanation it is necessary to make use of an experimental fact established quite independently, ***viz.*** that the efficiency of an ***atom*** of a substance as a scatterer or reflector of X-rays is proportional to the atomic weight of the atom, the heavier the atom the more intense the reflection. The suggestion in regard to the spectra from the (111) face of NaCl is, therefore, that the alternations in intensity are due to alternate layers or planes of chlorine atoms, separated by layers of sodium atoms. How this explains the observed results will be clear in a moment. On this view *the real unit of matter, in crystal structure, is the atom itself, and crystal planes are atom-bearing planes. The idea of the molecule in a crystal is thus done away with,* any given sodium atom, for example, being surrounded by six equidistant chlorine atoms none of which can be said to belong particularly to the sodium atom. The crystal as a whole must be looked upon as one huge molecule represented by the formula $(NaCl)_n$.



(*c*) Diagram of Rock-salt Spectra.

FIG. 33. (After Bragg, *Chemical Society Transactions*, 1916

Let us construct a face-centred space lattice unit for NaCl, denoting the sodium atoms by white spheres, the chlorine by black (Fig. 34 A). We see at once that the (100) and (110) planes contain both kinds of atoms, and successive planes parallel to these surfaces are identical in composition. These planes function, therefore, in a normal manner, giving rise to spectra, the intensity of which progressively diminishes as the "order" increases. The spacing of these two planes is shown in Fig. 34 B. When we turn to the (111) planes, however, we see that these are composed *alternately* of sodium atoms only and chlorine atoms only. Now, as far as the reflection spectra are concerned, the true distance $d_{(111)}$ between successive planes is from like plane to like plane, *i.e.* from the first plane containing sodium *or* chlorine atoms alone to the next one containing sodiums or chlorines alone. Half way between two like chlorine planes we find a sodium plane. The angle of the first reflection is given by $\lambda = 2d_{111} \sin \theta_1$, where $d_{(111)}$ is the distance between two chlorine planes, say. If there were only chlorine planes present the spectra would diminish regularly in intensity. But in between each chlorine plane we have another reflecting plane, the sodium plane, which for the first order spectrum or reflection gives rise

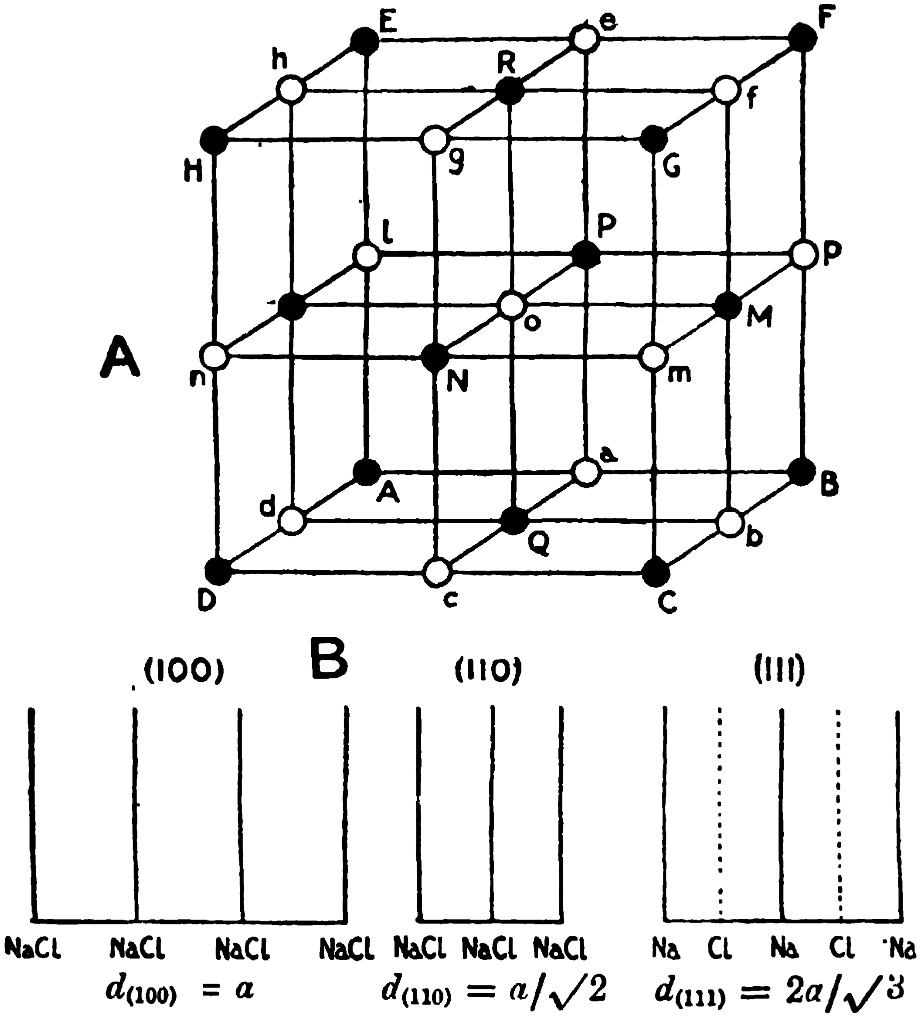


FIG. 34. (From Bragg's *X-Rays and Crystal Structure*, G. Bell & Sons.)

to waves just out of step with, *i.e.* in opposite phase to, the waves reflected from the chlorine planes. That is, the intensity of the first reflection from the chlorines is partly destroyed, and the same is true of the third, fifth, and higher odd orders. On the other hand, the second, fourth, and higher even orders are enhanced, for at these positions the chlorine planes and the sodium planes reinforce one another, the reflected waves from each kind of plane being in the same phase. This alternate enhancement and diminution in intensity is a well-known phenomenon in the ordinary diffraction of light when the grating is ruled not with even spacing, but with alternate broad and narrow lines. The whole phenomena connected with sodium chloride X-ray spectra can be satisfactorily explained, therefore, on the assumption that the fundamental lattice is face-centred, and that the points of the lattice represent chlorine atoms and sodium atoms alternately. This explanation is verified by NaBr and KBr respectively.

A very interesting case is that of KCl. The spectra obtained from a crystal of this substance is apparently identical with those which we would anticipate on the basis of the *simple*, not the face-centred, cube lattice. The great similarity between KCl and NaCl, in almost every, property, suggests very strongly, however, that the fundamental lattice is the same for both, namely, the face-centred lattice. The explanation of the apparent anomaly is very simple, and indeed serves to substantiate the conclusions already arrived at. The atomic weights of chlorine and potassium are not very different, and the X-rays are unable, so to speak, to detect any difference between the two kinds of atoms. If we turn to Fig. 34 A and imagine all the atoms identical, it is evident that the face-centred arrangement has become a simple cube arrangement. In the (111) face of KCl the atomic weights are so nearly identical that the reflected intensities are nearly identical also, with the result that the odd orders are completely cut out, for as we have seen, in the case of odd orders of the spectra, successive planes oppose each other's effects. This is the reason for the KCl spectrum corresponding apparently to the simple cube lattice. With KCl the structure is really face-centred, but the face-centred characteristics are masked by the fact that the two kinds of atoms composing the substance have nearly the same mass. It is, of course, only the (111) face spectra which allow us in general—in cubic crystals—to distinguish between the simple cube lattice and the face-centred lattice. The (100) and (110) faces give the same effect in either case as we have seen.

An important general conclusion can now be drawn from the nature of the spectra obtained from any face. If the intensities of successive reflections, *i.e.* the orders, do not diminish regularly, but exhibit abnormal values, it may be inferred at once that the successive planes are different as regards spacing and constitution.

Returning to the case of NaCl, it is evident that if we assume the face-centred structure, we can calculate the relative spacings between each atom. Knowing at the same time the density of a crystal and the mass of each atom, we can easily calculate the absolute distance of the atoms apart in the various directions. This gives us the quantity d. From this we can further calculate the wave-length of the X-ray, the spectra of which we have observed. For rock salt $d(100) = 2{\cdot}8 \times 10^{-8}$ cm.

Let us now consider another substance, zinc blende, ZnS, which likewise crystallises in the regular system. The X-ray spectra obtained from this substance are shown in the lower portion of Fig. 35.

The crystal is built up on the face-centred lattice, as is shown by the relative positions of the first order spectra from the three faces 100, 110, and 111, but there are certain peculiarities which require further consideration. In the case of the (100) planes, the odd orders are relatively weak compared with the even; the spectra from the (110) face are normal in behaviour; and in the (111) planes the second order is abnormally weak. W. H. and W. L. Bragg have shown that this behaviour can be explained by the structure shown in Fig. 36 A, in which the dark spheres represent Zn atoms, the white spheres sulphur atoms.

Since the (110) planes are normal, in that the spectra decrease regularly as the order increases, these planes must all be of the same kind, that is they must contain equal numbers of zinc and sulphur atoms. This is indicated in the figure, the sulphur atoms being placed centrally inside *alternate* cubic spaces. If we imagine the lattice extended it is evident that the sulphur atoms also form a face-centred lattice pushed into or interpenetrating the zinc lattice. The 100 planes yield a very weak first order spectrum, just as do the 111 planes. That is, there is interference, and we infer that in both cases we must have alternate planes of zinc alone and of sulphur alone. This is also exhibited by the Fig. The composition of the planes and their relative spacing in the case of the three faces 100, 110, and 111 are shown diagrammatically in Fig. 36 B. It will be observed that the 111 planes are of a new type in which the distance between successive zinc layers is four times that between a zinc layer and the next sulphur layer. With this arrangement it can be shown that the second order spectrum will be very much weakened, and the resulting spectra will agree with those observed from this face.

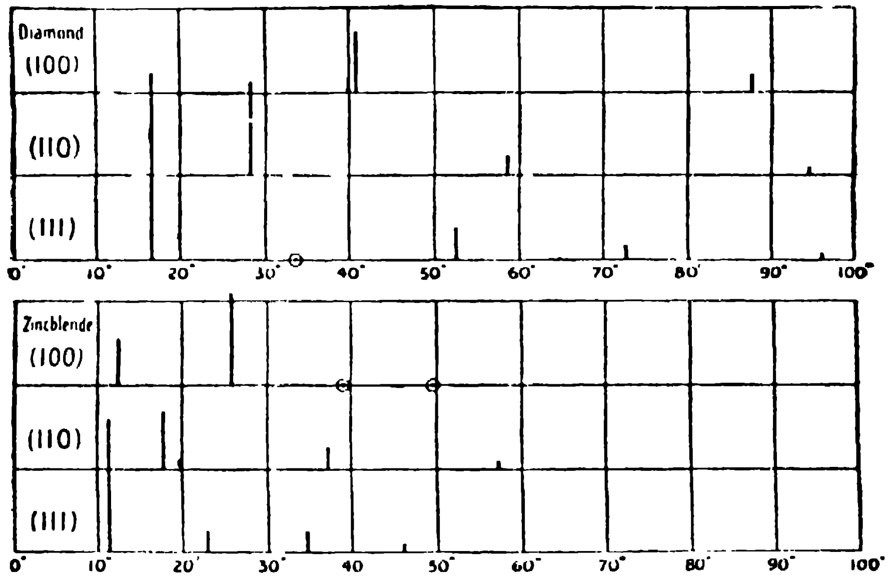


FIG. 35. (From Bragg's *X-Rays and Crystal Structure*, G. Bell & Sons.)

One further example of the method may be mentioned, namely, the determination of the structure of the diamond. The spectra obtained from a diamond are shown in Fig. 35, upper half. They are very similar to the spectra from ZnS, and we can account for the facts by regarding the diamond as built up on two intersecting or interpenetrating face-centred lattices related to one another in exactly the same way as the zinc lattice and sulphur lattice in zinc sulphide. The structure of the diamond is therefore represented by Fig. 36 A, carbon atoms taking the place of both zinc and sulphur atoms. Interference occurs just in the same places as it occurs in zinc blende, but now that all the atoms are similar, the interference is not partial, but complete. Thus from the 100 face, we obtain no first or third order spectra at all. From the 111 face we obtain no second order spectrum. It is a very striking and interesting fact that the structure attributed to diamond involves the further conclusion that each carbon atom is at the centre of a tetrahedron, and further that when a sufficient number of carbon atoms are considered, they form an interlocked arrangement of six-membered rings analogous to that of benzene. The latter arrangement is shown in the upper half of Fig. 37.

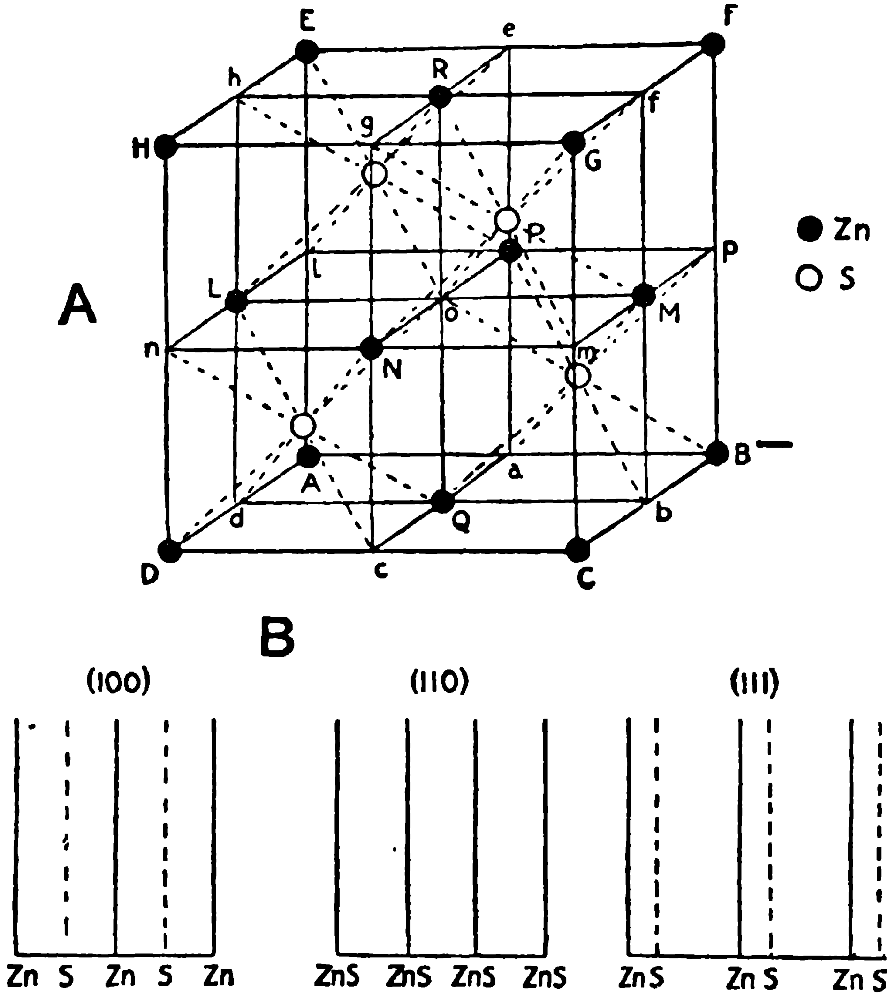
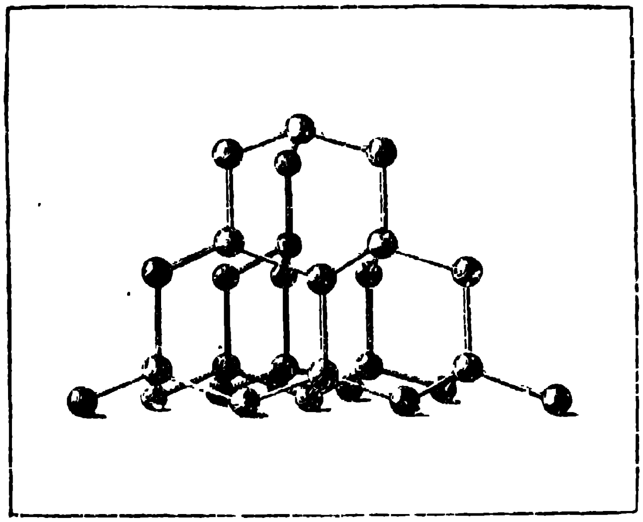
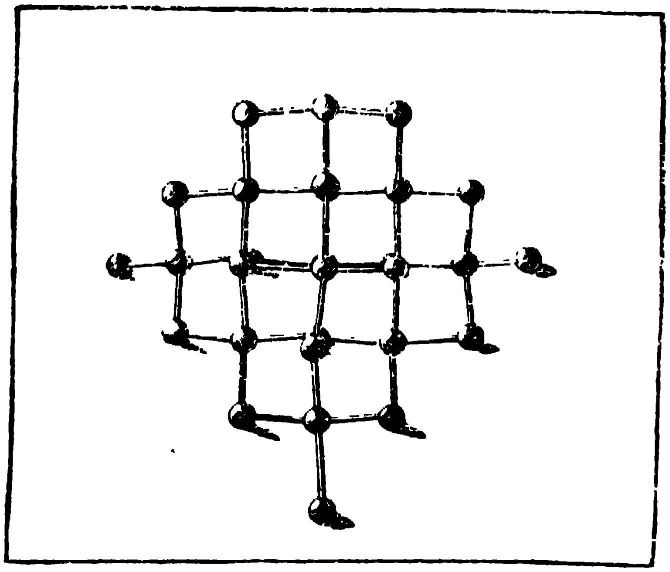


Fig. 36. (From Bragg's *X-Rays and Crystal Structure*, G. Bell & Sons.)

Numerous other crystals, such as fluorspar, iron pyrites, spinel, calcite, dolomite, etc., have been investigated and their structure elucidated by the X-ray method. An account will be found in the book referred to, *X-Rays and Crystal Structure*, as well as in the original papers.



Model of the Diamond. The (111) Planes are Horizontal.



Model of the Diamond. The (110) Planes are Vertical and Horizontal.

FIG. 37. (After Bragg.)

More recently X-ray methods have been applied by Sir W. Bragg and his school to the structure of organic compounds of various kinds, *cf. inter alia*, *Proc. Physical Soc.*, **34**, Part I., 1921 ; *Trans. Chem. Soc.*, **123**, 2043, 3152, 3156, 1923.

Moseley's relation in regard to X-ray spectra is dealt with in Vol. III.

Applications of the Braggs' work to other physico-chemical problems have been made by Langmuir (*cf.* Chap. X., this volume).

CHAPTER III.

Chemical equilibrium in homogeneous systems (from the kinetic standpoint)—Gaseous systems—Deduction of the law of mass action—Reactions (in gaseous systems) involving no change in the total number of molecules—Reactions involving a change in the number of molecules—Effect of change of temperature and pressure upon the equilibrium constant.

INTRODUCTORY.

THE reason *why* a chemical reaction proceeds cannot be given in terms of the kinetic or molecular theory. From very early times the idea of affinity or chemical attraction between different kinds of matter had been generally recognised; the power of one body A to displace another B from a compound BC being attributed to the existence of a greater "affinity" between A and B than that between B and C. A good account of the historical evolution of the doctrine of affinity will be found in Mellor's *Chemical Statics and Dynamics.*[1] It is only relatively recently, however, that a more precise concept of affinity has been brought forward by van 't Hoff. This will be discussed in some detail in Vol. II. of this work. For the present we can only state that the reason why a reaction proceeds is directly connected with the energy of the system—not simply the kinetic energy of the particles, for indeed if the temperature of the system be kept constant throughout the reaction the kinetic energy of the particles will remain constant. We must defer consideration of the point until we are familiar with the principles of thermodynamics. It will be seen later that the chemical change is connected with a certain function of the system called the "entropy," the tendency of which is always to reach a maximum. It is an equivalent statement to say with regard to a reaction which proceeds at constant temperature and volume, that the change goes on until the "free-energy" of the system reaches a minimum. For the present, however, we simply accept the *fact* that a reaction does go until the final point is reached. When a reaction does not go completely, *i.e.* when the final point corresponds to a state of affairs in which the system contains some new products ("resultants"), as well as some of the initial substances ("reactants"), this point is known as the "equilibrium point" of the reaction under the given conditions of temperature and pressure. It is our present business to find out what principles govern this equilibrium in the case of reactions occurring in homogeneous systems. A homogeneous system is one which consists of a single phase or portion of matter physically identical at all parts, *e.g.* a mixture of gases. A heterogeneous system, on the other hand, is one which consists of two or more homogeneous parts, *e.g.* liquid water in contact with water vapour.

---

[1] Sir William Ramsay's series of "Textbooks of Physical Chemistry".

The first important work carried out upon reactions in homogeneous systems was that of Wilhelmy (1850), (*Poggendorff's Annal.*, **81**, 413, 499, 1850; *Ostwald's Klassiker*, No. 29), who measured the rate of the inversion of cane sugar $C_{12}H_{22}O_{11}$ in aqueous solution into dextrose and lævulose under the catalytic action of a small quantity of acid (hydrochloric or nitric). A "catalyst" (Berzelius) is a substance which has the property of hastening on a reaction without itself taking any definite part in the reaction. In the above case there is just as much acid remaining at the close of the reaction as there was at the beginning. We may, therefore, omit consideration of the catalyst as far as the stoicheiometric equation representing the reaction

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{dextrose.}}{C_6H_{12}O_6} + \underset{\text{lævulose.}}{C_6H_{12}O_6}$$

is concerned. Cane-sugar solution rotates a beam of polarised light to the right, that is cane sugar is dextro-rotatory, whereas the mixture of dextrose and lævulose is lævo-rotatory. Using a polarimeter Wilhelmy determined the rate of the reaction from the change in the angle of rotation at different time intervals. (By boiling the solution for some time the cane sugar is completely inverted, and the angular reading of the polarimeter given with this solution indicated the "final" point in terms of the polarimeter readings.) Wilhelmy made the assumption that the rate at which the inversion took place, that is, the quantity inverted in unit time, is proportional to the quantity of cane sugar still uninverted in the solution. This important assumption of Wilhelmy is the basis of the law of mass action. If the time be expressed by t and the quantity of sugar inverted after any given time be x, the velocity of inversion is $\frac{dx}{dt}$. This quantity $\frac{dx}{dt}$ is, according to Wilhelmy, proportional to the quantity of cane sugar remaining, which may be represented by $(a - x)$, where a is the original quantity of cane sugar when $t = 0$. Hence Wilhelmy's equation is—

$$\frac{dx}{dt} = k(a - x),$$

where k is a proportionality factor called the "velocity constant" of the reaction. On integration one obtains—

$$k = \frac{1}{t} \log_e \frac{a}{a - x} \text{ or } k_1 = \frac{1}{t} \log_{10} \frac{a}{a - x}$$

where $k = 2{\cdot}303k_1$.

Wilhelmy was the first to construct the differential equation quoted above for the calculation of a chemical reaction velocity.

Using nitric acid as the catalyst (at 15° C.) Wilhelmy succeeded in verifying the above equation experimentally, as will be seen from the figures in the following table:—

t (in Minutes).	$a - x$ in Polarimeter Readings.	Log $\frac{a}{a-x}$.	$k_1 = \frac{1}{t} \log_{10} \frac{a}{a-x}$.
0	65·45	—	—
45	56·95	0·0605	0·00134
90	49·45	0·1217	0·00135
150	40·70	0·1981	0·00132
210	33·70	0·2880	0·00137
270	26·95	0·3851	0·00142

The (approximate) constancy in the values of k_1 is evidence for the validity of Wilhelmy's theory.

The idea of *reversibility* in chemical reactions which had been suggested by Berthollet was taken up at a later date by Malaguti (1853), (*Annales Chim. et Physique* [3], **37**, 198, 1853; **51**, 328, 1857), who expressed the fundamental idea that chemical equilibrium—when it does occur—is due to the balance set up between two opposing reaction velocities in opposite senses. Malaguti as a matter of fact based his conclusion upon a heterogeneous not a homogeneous reaction, though the existence of equilibrium, as we shall see shortly, is more directly and conveniently demonstrated by some reactions occurring in homogeneous systems. Malaguti gave the first satisfactory explanation of a reversible reaction which had been observed by Marggraf in the eighteenth century, namely, the partial transformation of barium sulphate into barium carbonate and alkali sulphate by the addition of alkali carbonate, and the inverse reaction, namely, the production of barium sulphate by the addition of alkali sulphate to barium carbonate. Meanwhile, considerable advance had been made upon the subject of heterogeneous equilibrium in the case of solids in contact with gaseous decomposition products, notably in the case of calcium carbonate (solid) which on heating gives lime (solid) and carbonic acid gas, according to the equation—

$$CaCO_3 = CaO + CO_2.$$

Since calcium carbonate can be produced by bringing carbonic acid gas into contact with lime, an equilibrium state must be reached. Denoting the direction of a reaction by an arrow pointing either to left or right, it is usual to denote that such an equilibrium point is reached by rewriting the stoicheiometric equation in the form

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

As early as 1837, Aimée (G. Aimée, reprint *Journal Physical Chem.*, **3**, 364, 1899) stated that "when a body is decomposed by heat, it is not the pressure of any gas or vapour chosen at random which can stop its decomposition; it is the gas which arises from the decomposition which alone can act". This pressure, which is reached by the gaseous product (or products) so that the system is in equilibrium at a given temperature, is known as the "dissociation pressure" of the solid substance. The further work of Groves,[1] St. Claire Deville,[2] and H. Debray,[3] upon dissociation pressures and equilibrium points, yielded the following important conclusions:—

1. The dissociation pressure of a solid is constant at a given temperature.
2. The dissociation pressure increases with the temperature.
3. The dissociation pressure is independent of the amount of solids present (as long, of course, as there remains any of the original undecomposed solid).

The work which led, however, to the complete acceptance of the principle of equilibrium and a clear formulation of the law of mass action was that of Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.*, [3], **65**, 385, 1862; **66**, 5, 1862; **68**, 225, 1863); of Harcourt and Esson (*Phil. Trans.*, **156**, 193, 1866; **157**, 117, 1867; **186**, 817, 1895); and especially from the theoretical standpoint the work of Guldberg and Waage (1864), (*Etudes sur les affinités chimiques*, Christiania, 1867; *Journ. prakt. Chem.* [2], **19**, 69, 1879; Ostwald's *Klassiker*, No. 104).

The Law of Mass-Action (Guldberg and Waage).

The law of Mass-Action states that the rate at which a substance reacts is proportional to the *active mass* of the substance; and further that when chemical equilibrium is established this is due to opposing reaction velocities neutralising one another.

This law can be deduced from a kinetic molecular standpoint as well as from the standpoint of thermodynamics. We shall confine ourselves for the present to the kinetic method of deduction.

First of all, the term "active mass" requires some explanation. To obtain a simple idea of this term we must consider it as applying to reactions between gases in the first instance. (It will be shown later that it applies to reactions between substances dissolved in a solvent as well.) By "active mass" Guldberg and Waage understood what is usually termed the "molecular concentration" of the given substance, *i.e.* the number of molecules in a given volume of the gas or in the more frequently employed units, the number of gram-molecules per liter, or any term proportional to this, such as partial pressure.

Consider a simple type of reaction occurring in a homogeneous gaseous system at a given temperature. Let one molecule of a substance A react with one molecule of a substance B to produce one molecule of C plus one molecule of D, all these being gaseous substances. The ordinary or stoicheiometric equation representing the reaction is—

---

[1] Groves, *Phil. Trans.*, 137, 1, 1847.

[2] Deville, *Comptes Rendus*, 1857-1864, and *Leçons sur la dissociation*, Paris, 1866.

[3] Debray, *Comptes Rendus*, **64**, 603, 1867.

$$A + B = C + D.$$

If the reaction is one which reaches an equilibrium point at some stage—and all homogeneous gaseous reactions must do so, although in some cases the position of the equilibrium lies so far over to one side that the system consists *practically* of either reactants or resultants alone—the equilibrium state may be represented on the van 't Hoff notation by—

$$A + B \rightleftarrows C + D.$$

It is usual to denote the concentrations of these substances by the symbols C_A, C_B, C , C_D, or by simply enclosing the chemical symbol in a square bracket—$[A]$, $[B]$, $[C]$, $[D]$. These symbols denote concentration terms in general. Let us suppose the reaction has gone on until the equilibrium point is reached, at which point the concentration terms possess "equilibrium values," and may be denoted by C_{eA}, C_{eB}, C_{eC}, C_{eD}, or $[A]_e$, $[B]_e$, $[C]_e$, $[D]_e$, (e is simply a suffix indicative of equilibrium).

Now the rate at which A and B are combining is taken to be proportional to the *product* of their concentrations, *i.e.* at the equilibrium point the rate of combination is proportional to $C_{eA} \times C_{eB}$, or is *equal to* $k_1 C_{eA} \times C_{eB}$, where k_1 is a proportionality factor, namely, the velocity constant of the reaction from left to right. The employment of the product of the concentration terms and not any other function (such as their sum, for example) may be justified by considering a simple actual case.

"Suppose[1] we have a mixture in equal volumes of hydrogen and chlorine. A certain number of collisions in which an H_2 molecule strikes one Cl_2 molecule will occur in a second; and in some of these collisions combination will take place. Now let the concentration of the hydrogen be doubled, then twice as many H_2 molecules will collide with a Cl_2 molecule per second, and twice as much HCl will be formed. If the concentration of chlorine alone be doubled, the same effect will be produced, so that, if both concentrations are doubled, say, by compressing the gaseous mixture into half the volume, then four times as many collisions will occur in unit volume in unit time, and the velocity of the reaction, *i.e.* the amount of combination per second, will be quadrupled." The velocity therefore with which the reaction takes place is proportional to the *product* of the concentration terms.

To return to the reaction $A + B \rightleftarrows C + D$, it is evident that A and B combine (that is, disappear as such and appear as $C + D$) in equivalent amounts, namely, the disappearance of *one* molecule of A for one molecule of B. That is, A and B disappear at the same rate. Hence we can write in general—

$$\text{rate of disappearance of A and B} = k_1 C_A \times C_B$$

---

[1] Lehfeldt, *Textbook of Physical Chemistry*.

or at the equilibrium point—

$$\text{rate of disappearance of A and B} = k_1 C_{eA} \times C_{eB}$$

and this velocity or rate must be identical with the rate of *formation* of C and D. In exactly the same way we see that the rate of *disappearance* of C and D (to produce A and B) is given by the expression—

$$k_2 C_C \times C_D$$

where k_2 is the proportionality factor or velocity constant of the reaction from right to left. At the equilibrium point we have—

$$\text{rate of disappearance of C and D} = k_2 C_{eC} \times C_{eD}$$

and this rate is identical with the rate of formation of A and B at the equilibrium point. Now at the equilibrium point it is clear that just as many molecules of A and B are disappearing per second as are formed per second. Hence at the equilibrium point we can equate the two velocity expressions given above. That is—

$$k_1 C_{eA} \times C_{eB} = k_2 C_{eC} \times C_{eD}$$

or

$$\frac{C_{eC} \times C_{eD}}{C_{eA} \times C_{eB}} = \frac{k_1}{k_2} = K$$

where K is called the "equilibrium constant" of the reaction. We may equally well define the equilibrium state by employing the reciprocal of K—call it K_1—in which—

$$K_1 = \frac{C_{eA} \times C_{eB}}{C_{eC} \times C_{eD}}.$$

It will be observed that K (or K_1) is simply the ratio of two velocity constants, k_1 and k_2, that is K is the ratio of the velocity constant of the reaction left to right, to the velocity constant of the reaction right to left. Since k_1 and k_2 always vary with the temperature and not necessarily to the same extent, it is evident that their ratio K, the equilibrium constant, may also vary with the temperature. In certain cases also which will be discussed later in connection with liquid systems, K varies with the pressure of the system. The problem of the shift of equilibrium with temperature and pressure can only be satisfactorily considered, however, from the thermodynamic standpoint. It is governed by the "principle of mobile equilibrium," first introduced into chemistry by Le Chatelier and by Braun. It should be remembered therefore that when we speak of the equilibrium constant of a reaction, and assign a numerical value to it, it is necessary to state the temperature for which the numerical value holds.

To return to the equilibrium equation, it is sometimes convenient to express it in logarithmic form, *viz.*—

$$\log C_{eC} + \log C_{eD} - \log C_{eA} - \log C_{eB} = \log K$$

or, in general—

$$\Sigma \log C = \log K$$

where C denotes concentration in general, and $\Sigma \log C$ denotes the algebraic sum of the logs of all such concentration terms.

There are some points which still require further consideration. Thus we must be careful to distinguish between equilibrium concentration and any other concentration, say, the initial concentration. Let us consider the same reaction once more. Suppose we start with a gram-molecules of gas A, and b gram-molecules of gas B in a vessel of volume v. Then the *initial* concentration of A is $\frac{a}{v}$, and the initial concentration of B is $\frac{b}{v}$. These are *not* equilibrium concentrations (unless indeed we have previously added the requisite amount of C and D to the vessel so that the initial state is actually made identical with the equilibrium state). Suppose A and B are alone present in the vessel. Reaction takes place, and let us suppose that equilibrium is reached when ϵ molecules of A have disappeared. Since the reaction is a very simple one, namely, *one* molecule of A reacting with *one* molecule of B to give *one* molecule each of C and D, it follows that when ϵ molecules of A disappear, the same number ϵ molecules of B will likewise disappear and ϵ molecules of both C and D will be produced. At the equilibrium point we have therefore $(a - \epsilon)$ molecules of A remaining, $(b - \epsilon)$ molecules of B, and ϵ molecules of C, and ϵ molecules of D. Since the volume v remains constant, the equilibrium concentration terms are—

$$\frac{a-\epsilon}{v} \text{ for A,} \quad \frac{\epsilon}{v} \text{ for C,}$$

$$\frac{b-\epsilon}{v} \text{ for B,} \quad \frac{\epsilon}{v} \text{ for D.}$$

Hence the equilibrium constant K is given by—

$$K = \frac{\frac{\epsilon}{v} \times \frac{\epsilon}{v}}{\frac{a-\epsilon}{v} \times \frac{b-\epsilon}{v}} = \frac{\epsilon^2}{(a-\epsilon)(b-\epsilon)}.$$

Let us now consider another type of reaction, in which more than one molecule of A—say two molecules—react with one molecule of a second substance B, giving rise, say, to two molecules of C and one molecule of D. The reaction is therefore represented by—

$$2A + B = 2C + D$$

and the equilibrium point by—

$$2A + B \rightleftarrows 2C + D.$$

The rate of combination of the 2A and B depends on the kinetic basis upon the number of effective collisions between these substances in a given time. In the first reaction considered $(A + B \rightarrow C + D)$

combination could occur when *one* molecule of A collided with *one* molecule of B. In the present case it is necessary that *two* molecules of A come into contact simultaneously with *one* molecule of B, so that the reaction from left to right may proceed. The rate of the reaction will therefore not simply depend upon the product of the concentration of A into the concentration of B, but will be governed by a somewhat more complicated function. The simplest way of considering such a reaction—though it is somewhat artificial—is to rewrite the equation as follows:—

$$A + A + B = C + C + D$$

and to regard the two A terms as separate entities as far as reactivity is concerned. The rate of reaction from left to right is therefore given by $k_1C_A \times C_A \times C_B$ or $k_1C^2{}_A \times C_B$. Similarly the rate of reaction from right to left is $k_2C^2{}_C \times C_D$. Hence the equilibrium constant K is given by—

$$K = \frac{k_1}{k_2} = \frac{C^2_{eC} \times C_{eD}}{C^2_{eA} \times C_{eB}}$$

In an exactly similar manner we may deal with more complicated reactions still, the most general type of chemical reaction being represented by the stoicheiometric equation—

$$\nu_1A_1 + \nu_2A_2 + \text{etc.} = \nu_1'A_1' + \nu_2'A_2' + \text{etc.}$$

which corresponds to the equilibrium relation—

$$K = \frac{C^{\nu_1'}_{eA_1'} \times C^{\nu_2'}_{eA_2'} \times \ldots}{C^{\nu_1}_{eA_1} \times C^{\nu_2}_{eA_2} \times \ldots}$$

or in the more convenient logarithmic form—

$$\Sigma\nu \log C = \log K.$$

As already mentioned, one meets with the above mass action expression in the inverted form. It is purely a matter of convention.

Another point requires a little consideration, namely, the use of the term "active *mass*". It will have been observed that the essential quantity appearing in the foregoing treatment is concentration or mass per given volume. The use of the term "mass" in the expression "mass action" is therefore rather unfortunate. The expression should more correctly take the form "concentration action". This will be clearly brought out when we come to study heterogeneous equilibrium such as the dissociation of calcium carbonate, in which it will be seen that the equilibrium point as measured by the concentration (or partial pressure) of the CO_2 is absolutely independent of the total *mass* of the solid carbonate—in fact, that the *active mass* of a solid is a *constant* whether the *actual* quantity present be great or small.

Having now considered the principle of mass action from the kinetic standpoint, we may pass on to consider some gaseous reactions in more detail.

HOMOGENEOUS GASEOUS REACTIONS.—FIRST-TYPE GAS REACTIONS, *i.e.* reactions in which there is *no* change in the *total* number of molecules in the system.

Reactions of this type may be illustrated by the classic case of the dissociation of hydriodic acid according to the equation—

$$\underset{\text{(gas)}}{2\text{HI}} = \underset{\text{(gas)}}{\text{H}_2} + \underset{\text{(gas)}}{\text{I}_2}$$

in which it will be seen that there are just as many molecules on the one side of the equation as on the other. The temperature is supposed to be sufficiently high so that the iodine is entirely in the state of vapour.

In purely gaseous reactions it has been found convenient to express the active mass not as a concentration term directly but in terms of the partial pressure of each component. The partial pressure of a gas in a gaseous mixture is proportional to the concentration of the gas. Thus in the above case if we write p_{eHI} for the partial pressure of the unchanged HI when equilibrium is reached (p_e = equilibrium partial pressure) at a given temperature, then C_{eHI} is proportional to this quantity. That is $C_{eHI} = kp_{eHI}$. Similarly $C_{eH_2} = kp_{eH_2}$, and $C_{eI_2} = kp_{eI_2}$, so that the mass action expression is—

$$K = \frac{C_{eH_2} \times C_{eI_2}}{C^2_{eHI}} = \frac{kp_{eH_2} + kp_{eI_2}}{k^2p^2_{eHI}} = \frac{p_{eH_2}.p_{eI_2}}{p^2_{eHI}}.$$

This reaction has been very carefully studied by Lemoine (*Annales de Chim. et de Phys.* [5], **12**, 145, 1877), and at a later date and more thoroughly by Bodenstein and his pupils (*Zeitsch. phys. Chem.*, **13**, 56, 1893; **22**, 1, 1897; **29**, 295, 1899). We shall therefore consider briefly some of Bodenstein's data upon this reaction, as these afford very satisfactory experimental confirmation of the validity of the law of mass action itself. Evidently the way to set about to verify such a law would be by carrying out a series of experiments in which the initial quantities of the reactants are altered, and after allowing equilibrium to be established in all the cases at the same temperature, one could calculate from the analyses of the mixtures the respective values of the equilibrium constant and observe if agreement were obtained in the several cases. Another convenient way of demonstrating the same point is to carry out one or more experiments of the above kind, and so obtain a numerical value for the equilibrium constant, and then, by applying this value, calculate the quantity of some one of the components (say the HI), which should exist if the law is valid when equilibrium is reached in another experiment or series of experiments where new quantities of the reacting substances have been employed, and finally compare the found HI concentration with the calculated. The best method of demonstrating that a state of equilibrium really exists is to approach it from both sides. Thus, start with pure HI, allow a steady state to be reached at a certain temperature and calculate K.

Then start with H_2 and I_2 at the same temperature, and again allow the reaction to proceed until no further change is noticeable, and again calculate K. If the two values of K agree, the principle is proved very conclusively.

The following illustrates one of the lines of investigation pursued by Bodenstein in the case of the hydriodic acid decomposition equilibrium. Let us express the degree of decomposition of the pure HI by x; that is one grammole of HI is supposed to have reacted to such an extent that at equilibrium there are $(1 - x)$ moles of undecomposed HI, $\frac{x}{2}$ moles of H_2 and $\frac{x}{2}$ moles of iodine (vapour). [Note that *one* molecule of HI only gives rise to *one-half* a molecule of H_2 or I_2.] If the volume of the vessel be v, and one such gram-molecule of HI had been originally introduced into it, then the equilibrium concentration terms are—

$$\begin{array}{ccc} HI & H_2 & I_2 \\ \dfrac{1-x}{v} & \dfrac{x}{2v} & \dfrac{x}{2v}. \end{array}$$

$$\text{Hence } K = \frac{p_{eH_2} \times p_{eI_2}}{p^2_{eHI}} = \frac{C_{eH_2} \times C_{eI_2}}{C^2_{eHI}} = \frac{\dfrac{x^2}{4v^2}}{\dfrac{(1-x)^2}{v^2}} = \frac{x^2}{4(1-x)^2}.$$

Let us now consider the reverse reaction, starting from a mixture of H_2 and I_2, say a moles of iodine, and b moles of hydrogen in a volume v (which remains constant throughout the experiment), and let equilibrium be finally established when $2c$ moles of HI are formed. At the equilibrium we have therefore $(a - c)$ moles of I_2; $(b - c)$ moles of H_2; and $2c$ moles of HI. The equilibrium constant K is therefore given by the expression—

$$K = \frac{p_{eI_2} \times p_{eH_2}}{p^2_{eHI}} = \frac{\dfrac{a-c}{v} \times \dfrac{b-c}{v}}{\dfrac{4c^2}{v^2}} = \frac{(a-c)(b-c)}{4c^2}$$

which solved[1] for c gives—

$$c = \frac{a+b}{2(1-4K)} - \sqrt{\frac{(a+b)^2}{4(1-4K)^2} - \frac{ab}{1-4K}}.$$

The following data were obtained by Bodenstein: a and b denote the number of cubic centimetres of gaseous H_2 and I_2 (reduced to 0° C. and 760 mm.) that were contained in the glass bulb of about 13 c.c. capacity. [a and b therefore represent *initial* concentrations; they do not represent equilibrium values.] It will be observed that in this reaction there is no necessity to determine the volume of the vessel with any accuracy at all as far as the equilibrium equation is concerned, for the v term cancels. It is not so, however, in other types of reactions, as we shall see later. $2c$ denotes the quantity of HI formed expressed in the same units. Bodenstein actually determined directly the quantities $(a - c)$, $(b - c)$, and c (or $2c$).

---

[1] In solving such equations there is no doubt about the sign before the root, as only *one* solution gives a physically possible result. In the above case, for example, a + sign would yield values for c greater than $a + b$, which is, of course, impossible.

Temperature 357° C. (vapour of boiling mercury used as constant temperature bath).—The value of x was found experimentally to be 0·1946, the reaction considered being $2HI \rightarrow H_2 + I_2$. Hence K is calculated to be 0·01494. Using this value, $2c$ could be calculated for the series of experiments in which H_2 and I_2 formed the initial mixture, *i.e.* $H_2 + I_2 \rightarrow 2HI$.

a.	*b*.	*2c* Observed.	*2c* Calculated
2·59	6·63	4·98	5·02
5·71	6·22	9·55	9·60
10·40	6·41	11·88	11·68
26·22	6·41	12·54	12·34
23·81	6·21	12·17	11·98
22·29	6·51	12·71	12·68

Temperature 448° C. (sulphur vapour bath).—The value of x was found to be 0·2198. Hence K is calculated to be 0·01984. Note that at the higher temperature, x, and therefore K, has become larger, that is, the degree of decomposition of HI increases with the temperature. Using this value of K, $2c$ is calculated as before.

a.	*b*.	*2c* Observed.	*2c* Calculated.
2·94	8·10	5·64	5·66
5·30	7·94	9·19	9·52
9·27	8·07	13·47	13·34
14·44	8·12	14·93	14·82
27·53	8·02	15·54	15·40
33·10	7·89	15·40	15·12

Bodenstein's results confirm the theory in a very satisfactory manner.

An important feature of the above reaction is that it involves no volume change, for although the nature of the molecules differs, the pressure produced only depends upon the number per unit volume, and this remains constant. In the other type of reaction, in which the number of molecules changes during the reaction, we can indeed keep the system at constant volume, but it will be found that the total pressure is not the same at the beginning and at the end. Examples of this type will be considered later. As further examples of the above type of reaction, mention may be made of the following :—

The formation and decomposition of hydrobromic acid and hydrochloric acid—

$$2HBr \rightleftarrows H_2 + Br_2$$

(Bodenstein and Geiger, *Zeitsch. phys. Chem.*, **49**, 70, 1904);

$$2HCl \rightleftarrows H_2 + Cl_2$$

(Dolezalek, *Zeitsch. phys. Chem.*, **26**, 334, 1898).

Also the technically important reactions, namely, that dealing with the fixation of nitrogen from the air—

$$N_2 + O_2 \rightleftarrows 2NO$$

(Nernst, *Göttingen Nachrichten*, p. 261, 1904; Nernst, Jellinek, and Finckh, *Zeitsch. anorg. Chem.*, **45**, 116, 1905; **49**, 212, 1906; **49**, 229, 1906);

and the well-known water gas[1] equilibrium—

$$CO_2 + H_2 \rightleftarrows H_2O + CO.$$

For details of these reactions the reader is referred to Haber's *Thermodynamics of Technical Gas Reactions.*

As already pointed out, a consequence of the absence of volume change in the above cases is that for all such reactions the numerical value of the equilibrium constant is the same, whether we express the active mass of the components either in concentration terms (gram molecules per liter) or in partial pressure terms (atmospheres). This can be seen at once by inspection of the equilibrium mass action equation, because the proportionality factor k connecting partial pressure with concentration occurs as often in the numerator as in the denominator, and therefore vanishes. On the other hand, suppose one considers a reaction in which there is a change in the total number of molecules as the reaction proceeds, thereby causing a change in volume (if the external pressure be kept constant), the numerical value of K will not be the same when expressed in concentration and partial pressure terms respectively. Thus, take the case of the decomposition of nitrogen peroxide—

$$N_2O_4 \rightleftarrows 2NO_2.$$

In concentration terms—

$$K = \frac{C^2_{eNO_2}}{C_{eN_2O_4}}.$$

Now $C_{eNO_2} = kp_{eNO_2}$ and $C_{eN_2O_4} = kp_{eN_2O_4}$.

Therefore $K = \frac{k^2p^2_{eNO_2}}{kp_{eN_2O_4}} = \frac{kp^2_{eNO_2}}{p_{eN_2O_4}}.$

Writing $\frac{p^2_{eNO_2}}{p_{eN_2O_4}} = K_p$

we have $K = kK_p.$

---

[1] "Water gas" itself is produced by passing steam over heated carbon, thereby forming a mixture of CO_2, CO, H_2, and H_2O vapour. This mixture can be used as a gaseous fuel, since it gives out considerable heat when burnt with air.

Note.—Instead of writing K with the significance attached to it above, another convention has been adopted by Haber (on the ground that it gives more convenient numerical values), in which the equation of the reaction is so written as not to include any molecular number greater than unity, though at the same time this necessarily means the introduction of fractional molecular numbers. Thus the decomposition of hydriodic acid would be represented by $HI = \frac{1}{2}H_2 + \frac{1}{2}I_2$, and—

$$K_{Haber} = \frac{C_{eH_2}^{\frac{1}{2}} \times C_{eI_2}^{\frac{1}{2}}}{C_{eHI}}$$

which is evidently the square root of the previous K.

Let us return to the case of first-type gas reactions. One of the most important consequences of the characteristic absence of change in the total number of molecules is brought out when we consider what is *the effect of diluting* (i.e. *expanding*) *or concentrating* (i.e. *compressing*) *such a system.*

Suppose a certain mass of HI is brought into a vessel, and equilibrium is reached when the partial pressures are p_{eHI}, p_{eI_2}, p_{eH_2} respectively, the total pressure being, say, 1 atmosphere, so that

$$p_{eHI} + p_{eH_2} + p_{eI_2} = 1$$

the equilibrium constant K is—

$$\frac{p_{eH_2} \times p_{eI_2}}{p^2_{eHI}}.$$

Now suppose we compress the system so that the *total* pressure is now two atmospheres. This is the same as doubling the concentration, since the volume is only one-half its original size. Momentarily, therefore, in this case the partial pressures take on double their former values, and the expression becomes—

$$\frac{2p_{eH_2} \times 2p_{eI_2}}{4p^2_{eHI}}$$

which is identical with the former value. There is therefore no necessity for any "chemical" change to take place in the system in order that K may retain its former value. The state of things reached "momentarily" (*i.e.* at an imaginary period of time infinitely close to the moment when the alteration in the pressure of the system took place) is still an equilibrium state.

The fraction of HI dissociated or the degree of decomposition is therefore not altered in the slightest by the compression, nor would it have been altered, as may be easily seen, had we expanded the system, thereby decreasing all the partial pressures.

(In the second type of gas reaction, however, where there is a change in the number of molecules, it will be found that the "momentary state" is not an equilibrium state, but that some chemical change must take place in order to maintain K at its former numerical value.) In the hydriodic acid case no chemical change takes place on compression or rarefaction. The reasonableness of this conclusion may be demonstrated on the basis of the kinetic theory, as follows: ". . . before H_2 or I_2 can be produced, two molecules of HI must meet, and before the HI can be reformed a molecule of hydrogen must encounter a molecule of iodine vapour. The chances of each kind of encounter will be equally affected by a change in the concentration, so that the equilibrium established for one concentration will hold good at any other concentration. Although, therefore, the velocities [*i.e.* the $\frac{dx}{dt}$ terms, *not* the velocity constants] of the opposed reactions are altered by alteration in the concentration, they are altered to the same extent, and the position of equilibrium is unaffected" (Walker[1]). This has been proved experimentally by Bodenstein. Thus at 448° C. Bodenstein found the following values for x, the degree of dissociation:—

Total pressure (in atmospheres)	0·5,	1·0,	1·5,	2·0
x	0·2019,	0·2143,	0·2225,	0·2306

According to the theory, x should remain constant, and this is seen to be approximately the case. The apparent rise in x is very probably due, as Bodenstein has suggested, to adsorption of the HI by the walls of the vessel.

EFFECT OF TEMPERATURE UPON THE EQUILIBRIUM CONSTANT.

It has already been mentioned that K varies with the temperature. This, as will be seen in the thermodynamic treatment of the problem, is essentially due to the fact that heat is evolved or absorbed by the reaction. It may also be regarded from the kinetic standpoint as due to the fact that the velocity constants k_1 and k_2 $\left(K = \frac{k_1}{k_2}\right)$ vary with the temperature, and not necessarily to the same extent. To illustrate the extent of the variation of K in the case of the HI decomposition, a few of Bodenstein's values may be quoted. x again represents the degree of decomposition of the HI, so that $K = \frac{x^2}{4(1 - x)}$.

t° C.	T abs.	x.	K.
280	553	0·17803	0·01172
360	633	0·19700	0·01504
460	733	0·22535	0·02115
520	793	0·24483	0·02625

EXPERIMENTAL METHODS OF MEASURING HOMOGENEOUS EQUILIBRIA IN GASES.—FIRST-TYPE GAS REACTIONS.

The methods may be divided into three classes: (1) static methods, (2) dynamic methods, and (3) indirect methods.

---

[1] Professor James Walker's *Introduction to Physical Chemistry*.

(1) As an illustration of the static method, one may quote the following account of Bodenstein's measurements in connection with the HI, I_2, H_2 reaction.

A number of glass bulbs, each of about 15 c.c., are filled with HI gas at various pressures (½, 1, 1½, and 2 atmospheres) at room temperature, and the bulb sealed off. They were then heated in baths at known temperatures between 100° C. and 518° C. for given intervals of time. The bulbs were then removed, cooled as quickly[1] as possible, and opened under caustic potash, which dissolved the HI still remaining, as well as the iodine, the hydrogen remaining undissolved. Bodenstein then determined the volume of the bulbs, and hence the weight of HI originally contained in them. By measuring the quantity of hydrogen one could calculate the amount of I_2, and likewise the amount of HI decomposed. In another series of experiments, the bulbs were filled with known amounts of H_2 and I_2, reaction allowed to take place, the analyses being carried out in an analogous manner. The results of the two series of experiments—those in which the starting point is pure HI, and those in which the starting point is $H_2 + I_2$—are shown in the figure (Fig. 38). The abscissæ represent the duration of the experiment, ordinates the fraction of HI present on opening and analysing. Note that the points marked on the curves do *not* represent equilibrium values (until the horizontal portion is reached), but simply the quantities of HI present at arbitrarily chosen time intervals. The curves show that in the early stages the reaction proceeds rapidly, but gradually slows down as the equilibrium point is approached. Notice that the two curves eventually coincide, that is, the same position of equilibrium is reached[2] from both sides. At 448° C. the equilibrium point corresponds to a 22 per cent. decomposition of the HI.

(2) The dynamic methods of measuring equilibrium are particularly suitable for reactions occurring at a high temperature. The methods consist in allowing the reacting gas mixture to stream through a vessel kept at the required temperature, on passing out of which the gases are cooled as rapidly as possible. The chief difficulty is to get sufficiently rapid cooling. Since the gases are not, as a rule, in contact for a long time in the heated chamber, it has been found of the greatest advantage to employ some catalytic material in the heating vessel. If the catalyst is working properly, it has the property of hastening on a reaction without altering the equilibrium point, that is, the catalyst increases the velocity constants k_1 and k_2 of the direct and opposed reactions equally. The walls of the vessel have been shown by Bodenstein to act to a certain extent as a catalyst. Certain metals of the platinum group—

---

[1] This is known as chilling or freezing the equilibrium. It is assumed that the equilibrium ratios corresponding to the high temperature of the experiment have not had time to alter owing to the decrease in velocity as the temperature is quickly lowered.

[2] The effect of temperature on the rate at which equilibrium is reached is very marked. In this reaction at 440° C. the time is measurable in hours, at 350° C. in days and at 250° C. months are required.

especially platinum itself in a finely-divided form—have been found to be of great service as catalysts. In order to be certain that the composition of the emitted (and analysed) gas mixture really corresponds to the equilibrium in the reaction chamber, one must vary certain of the conditions as much as possible, *e.g.* the arbitrarily chosen composition of the initial mixture, the velocity with which the gas mixture is caused to stream through the hot chamber, and the duration of the experiment. The temperature of the hot vessel is, of course, kept constant. The verification of equilibrium having really been reached and determined, is best carried out by approaching the equilibrium point from both sides, as Bodenstein did in the case of the HI, H_2, I_2 reaction.

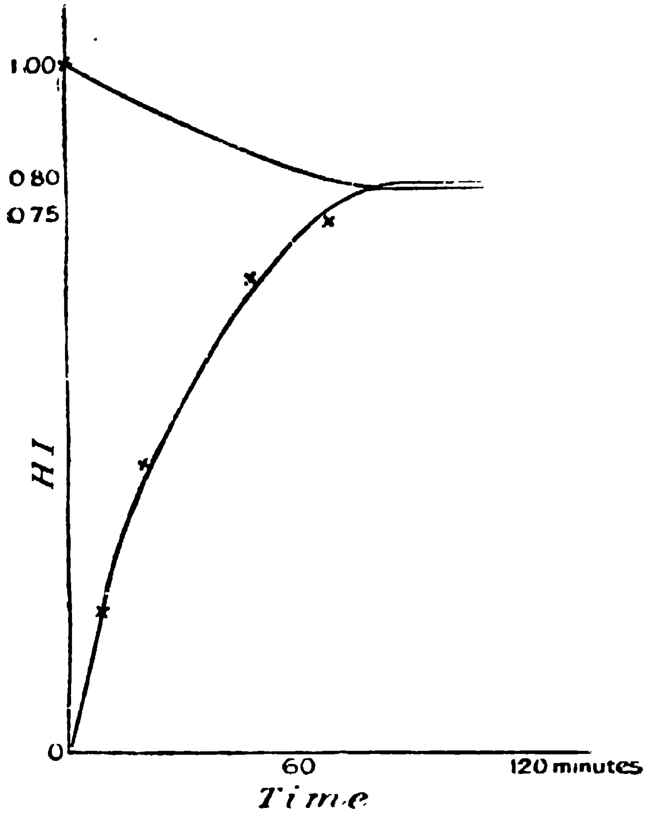


FIG. 38.

(3) The indirect method of determining equilibria—which, however, is less frequently resorted to than the direct—consists in measuring the reaction velocity constants k_1 and k_2 of the direct and opposed reactions, the equilibrium constant K being simply the ratio of these. These measurements have to be carried out at the earliest possible stage of the respective reaction. The reason of this will be clear when we come to discuss the chemical kinetics of opposed reactions.

SECOND-TYPE GAS REACTIONS,

i.e. those in which there is a change in the total number of molecules in the system during the reaction.

The simplest examples of this type are cases of gaseous dissociation. It is observed that while many gases and vapours give normal vapour densities—densities from which one can calculate molecular weights which are in agreement with the percentage composition of the substances as determined by analysis—many others give abnormal values, which can only be explained on the assumption that a certain number of the molecules have broken up into individuals of smaller molecular weight, thereby increasing the total number of individuals (*i.e.* increasing the volume if the pressure be kept the same), while the total *mass* of course remains the same. On raising the temperature of such a gas the density will naturally diminish, but it is found to diminish *more rapidly* than is to be expected on the kinetic theory when the rise in temperature only affects the distance of molecules apart without affecting their number. As illustrations of second type reactions, one may cite the decomposition of the halogens—

$$I_2 \rightleftarrows 2I \qquad Br_2 \rightleftarrows 2Br \qquad Cl_2 \rightleftarrows 2Cl.$$

The dissociation of iodine vapour has been much studied, especially by Victor Meyer (*Ber.*, **13**, 394, 1880), and recently by Starck and Bodenstein (*Zeitsch. Electrochem.*, **16**, 961, 1910). A similar reaction is the dissociation of nitrogen peroxide

$$N_2O_4 \rightleftarrows 2NO_2$$

(E. and L. Natanson, *Wied. Ann.*, **24**, 454, 1885; **27**, 606, 1886).

At still higher temperatures the NO_2 molecules partially dissociate into NO and O_2, according to the equilibrium equation—

$$2NO_2 \rightleftarrows 2NO + O_2$$

(Richardson, *Journ. Chem. Soc.*, **51**, 397, 1887).

Further, carbon dioxide dissociates at high temperatures, giving rise to an equilibrium represented by the equation—

$$2CO_2 \rightleftarrows 2CO + O_2$$

(Le Chatelier, *Zeitsch. phys. Chem.*, **2**, 782, 1888; Nernst and v. Wartenberg, *Zeitsch. phys. Chem.*, **56**, 534, 1906).

This reaction is of great importance in smelting furnace work.

Other examples are: The dissociation of water vapour—

$$2H_2O \rightleftarrows 2H_2 + O_2$$

(G. Preuner, *Zeitsch. phys. Chem.*, **42**, 50, 1903; Nernst and v. Wartenberg, *ibid.*, **56**, 534, 1906; Löwenstein, *ibid.*, **54**, 715, 1906; Langmuir, *Journ. Amer. Chem. Soc.*, **28**, 1357, 1906);

the dissociation of phosphorus pentachloride—

$$PCl_5 \rightleftarrows PCl_3 + Cl_2.$$

For the literature dealing with this reaction and the others mentioned, see Mellor's *Statics and Dynamics*.

In addition there are processes of great technical importance such as—

(*a*) The Deacon process of chlorine manufacture—

$$O_2 + 4HCl \rightleftarrows 2H_2O + 2Cl_2$$

(Vogel v. Falckenstein, *Zeitsch. phys. Chem.*, **59**, 313, 1907; G. N. Lewis, *Journ Amer. Chem. Soc.*, **28**, 380, 1906).

(*b*) The contact process of sulphuric acid manufacture, which depends essentially upon the reaction—

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

(Bodenstein and Pohl, *Zeitsch. Elektrochem.*, **11**, 373, 1905).

(*c*) The synthesis of ammonia—

$$N_2 + 3H_2 = 2NH_3$$

(Haber and v. Oordt, *Zeitsch. anorgan. Chem.*, **43**, 111; **44**, 341, 1905; also Haber and Le Rossignol, *Ber.*, **40**, 2144, 1907).

As an illustration of the gaseous dissociation of an organic substance one may cite that of ammonium carbamate, which dissociates at 60° C., according to the equation—

$$NH_2COONH_4 \rightleftarrows 2NH_3 + CO_2$$

For details of the technically important reactions referred to, the reader should consult Haber's *Thermodynamics of Technical Gas Reactions.*

Owing to the change in the number of molecules occurring in reactions such as the above, vapour density determinations have been frequently employed, since these show abnormal values from which the fraction dissociated and the dissociation constants can be obtained. Thus let us consider a gas which can undergo dissociation enclosed in a suitable vessel at constant temperature and suppose the density Δ measured. Suppose that we know the density δ of the gas if it were undissociated. This can be obtained by measuring the density at a lower temperature at which the gas is practically not dissociated at all. From this one can calculate by Gay-Lussac's Law, what the density would be at the higher temperature if no dissociation took place. Suppose, however, that each gram-molecule dissociates at the higher temperature to a fraction a, then instead of one individual in a given volume we have $(1 + a)$, supposing that the dissociation is of the simplest "binary" type, $A \rightarrow B + C$, *one* molecule giving rise to *two* smaller molecules or atoms. Now density is mass per unit volume, and the volume depends upon the number of individuals present, pressure being kept constant. Hence the density terms, *i.e.* the calculated and the observed, are inversely as the volumes containing the same mass. If Δ is the observed density at the higher temperature in question at which is the calculated or theoretical density, it follows that—

$$\frac{\Delta}{\delta} = \frac{1}{1 + a} \text{ or } a = \frac{\delta - \Delta}{\Delta}.$$

Now suppose one gram-molecule of the undissociated gas has been initially introduced into a vessel and the temperature raised, then when dissociation has taken place there are $(1 - \alpha)$ moles[1] of A, α moles of B, and α moles of C in a volume v, say, the corresponding concentration terms being $\frac{1-\alpha}{v}, \frac{\alpha}{v}, \frac{\alpha}{v}$.

The equilibrium mass-action equation is therefore—

$$\frac{C_{eC} \times C_{eB}}{C_{eA}} = \frac{\left(\frac{\alpha}{v}\right)^2}{\frac{1-\alpha}{v}} = \frac{\alpha^2}{(1-\alpha)v} = K_c.$$

The "dissociation constant" K_c can therefore be calculated from α, which in turn is obtained from density determinations.

It is sometimes convenient to express the dissociation constant in terms of another easily measurable magnitude, namely, the total pressure P exerted by the system when equilibrium is reached The expression also involves the δ and Δ terms.

Thus, taking the simple binary dissociation $A \rightarrow B + C$ as before, since the partial pressure of each molecular species depends upon the number of these particles in a given volume (*i.e.* the concentration), it will be seen since p_B is identical with p_C—these being equal partial pressure terms—that—

$$\frac{p_A}{p_B} \text{ or } \frac{p_A}{p_C} = \frac{\frac{1-\alpha}{v}}{\frac{\alpha}{v}} = \frac{1-\alpha}{\alpha}.$$

Hence $$\frac{p_A}{p_A + p_B + p_C} = \frac{1-\alpha}{1-\alpha+2\alpha} = \frac{1-\alpha}{1+\alpha}.$$

But $p_A + p_B + p_C$ = sum of all the partial pressures = total pressure P.

Hence $$\frac{p_A}{P} = \frac{1-\alpha}{1+\alpha},$$

or $$p_A = P\frac{1-\alpha}{1+\alpha}.$$

This expresses the partial pressure of the undissociated molecules in terms of the total pressure of the system. It is clear from this expression that the degree of dissociation varies with the total pressure of the system. Writing α in terms of δ and Δ, one obtains—

$$p_A = P\left(\frac{2\Delta}{\delta} - 1\right).$$

Similarly $$p_B = p_C = p_A\left(\frac{\alpha}{1-\alpha}\right) = P\frac{\alpha}{1+\alpha} = P\left(1 - \frac{\Delta}{\delta}\right).$$

---

[1] The term mole stands for gram-molecule.

The dissociation constant K_p—the constant obtained when partial pressure terms are employed instead of ordinary concentration terms (moles per litre), and which, as already pointed out, differs from K_c by a proportionality factor k—is given by the expression—

$$K_p = \frac{p_{eB} \times p_{eC}}{p_{eA}} = \frac{P(\delta - \Delta)^2}{\delta(2\Delta - \delta)}.$$

Expression for the dissociation constants K_c *and* K_p *in terms of the total pressure* P *when dissociation is small.*—Consider the reaction—

$$2H_2O \rightleftarrows 2H_2 + O_2$$

and suppose that a volume v contains altogether n moles of water vapour of which a number nx are decomposed into hydrogen and oxygen. That is, the degree of dissociation is x. The concentration of the undissociated water vapour molecules is—

$$\frac{n - nx}{v} \text{ or } \frac{n(1 - x)}{v}.$$

Now from the above reaction equation it will be seen that two molecules of H_2O give on dissociating two molecules of H_2 + one molecule of O_2. Hence nx molecules H_2O give rise to nx molecules of $H_2 + \frac{nx}{2}$ molecules of O_2. Therefore the concentration of the hydrogen is $\frac{nx}{v}$, and that of the oxygen is $\frac{nx}{2v}$. Hence—

$$K_c = \frac{C^2_{eH_2} \times C_{eO_2}}{C^2_{eH_2O}} = \frac{\frac{n^2x^2}{v^2} \times \frac{nx}{2v}}{\frac{n^2(1 - x)^2}{v^2}} = \frac{nx^3}{2v(1 - x)^2}.$$

The total pressure exerted by the system in equilibrium is P. Suppose that the partial pressure of each constituent obeys the gas law, and let us further assume, as is the case in the dissociation of water vapour even up to very high temperatures, that the degree of dissociation x is very small. Then $Pv = nRT$, since there are approximately n molecules of water vapour present. Hence $v = \frac{nRT}{P}$, and therefore—

$$K_c = \frac{Px^3}{2RT(1 - x)^2} \text{ or } K_c = \frac{Px^3}{2RT}$$

neglecting x compared to unity.

Further
$$\mathrm{K}_p = \frac{p^2_{e\mathrm{H}_2} \times p_{e\mathrm{O}_2}}{p^2_{e\mathrm{H}_2\mathrm{O}}} = \frac{(\mathrm{RT})^2 \,.\, \mathrm{C}^2_{e\mathrm{H}_2} \times \mathrm{RTC}_{e\mathrm{O}_2}}{(\mathrm{RT})^2 \,.\, \mathrm{C}^2_{e\mathrm{H}_2\mathrm{O}}}$$
$$= \mathrm{RT} \times \frac{\mathrm{C}^2_{e\mathrm{H}_2} \times \mathrm{C}_{e\mathrm{O}_2}}{\mathrm{C}^2_{e\mathrm{H}_2\mathrm{O}}} = \mathrm{RT} \times \mathrm{K}_c$$
$$= \mathrm{RT} \times \frac{\mathrm{P}x^3}{2\mathrm{RT}(1 - x)^2} = \frac{\mathrm{P}x^3}{2(1 - x)^2}.$$

Suppose as a special case that the total pressure of the system is one atmosphere, and that x is small compared to unity, then—

$$\mathrm{K}_p = \frac{x^3}{2}.$$

The dissociation constant can thus be calculated very simply from the degree of dissociation when the latter is small.

EXAMPLES OF SECOND-TYPE GAS REACTIONS.

It will be convenient now to consider a few of the reactions already mentioned in order to see how far the law of mass action is confirmed by the results obtained. A simple case is the dissociation of iodine vapour according to the equation $\mathrm{I}_2 \rightleftarrows 2\mathrm{I}$, recently investigated by Starck and Bodenstein (*Zeitsch. Electrochem.*, **16**, 961, 1910), who have shown the existence of definite equilibrium points at various temperatures, and have measured the equilibrium constants very accurately. The apparatus employed consisted of a quartz bulb fitted with a quartz manometer working on the same principle as the Bourdon gauge. The temperature range over which the measurements were carried out varied from 800° C. to 1200° C. The following are some of the values obtained:—

$\mathrm{K}_p = \dfrac{p^2_{e\mathrm{I}}}{p_{e\mathrm{I}_2}}$	Temperature (°C.).
0·0114	800
0·0474	900
0·165	1000
0·492	1100
1·23	1200

It will be observed that the dissociation into atomic iodine rapidly increases as the temperature is raised.[1] A similar phenomenon is exhibited by first-type gas reactions, *e.g.* the decomposition of HI.

---

[1] Starck and Bodenstein also calculated by thermodynamics the heat effect involved in the reaction, and showed that the thermal effects were in agreement with Nernst's heat theorem (see Vol. II., Chap. XIII.), which was not the case if one used V. Meyer's earlier data upon this reaction.

EFFECT OF PRESSURE ON THE DISSOCIATION IN SECOND-TYPE GAS REACTIONS.

At one and the same temperature the degree of dissociation, say, of iodine vapour, has been shown by experiment to be dependent upon the total pressure exerted by the vapour. The degree of dissociation increases the more dilute the system, *i.e.* the lower the pressure. It will be remembered that in first-type reactions (those involving no change in the total number of molecules) the effect of pressure upon the degree of dissociation was zero. This is the characteristic difference between first- and second-type reactions. The observed change of degree of dissociation in reactions involving a change in the total number of molecules is likewise satisfactory confirmation of the law of mass action, for such behaviour is predicted by the law. We may also anticipate the effect from the standpoint of the kinetic theory of gases. If we start with a given mass of gas occupying a certain volume under a given pressure, and increase the pressure, thereby reducing the volume, it seems reasonable to believe that this change does not affect the number of molecules of I_2 which dissociate per second, since each molecule dissociates, so to speak, of its own accord. The number of combinations per second of the separate iodine atoms will, however, be affected, for here each atom must meet a similar one in order to reform the original molecules of undissociated gas, and the number of times such combinations can take place will depend upon the collision frequency, this in turn upon the distance of the individuals apart, this again depending upon the volume occupied by the given mass of gas, and this finally depending upon the pressure. If therefore equilibrium is set up with a certain degree of dissociation under a given pressure, then on *increasing* the pressure (keeping the temperature constant, of course), the rate of combination of atoms will be favoured, the rate of dissociation of the molecules being left unchanged, with the result that the degree of dissociation will be *diminished*. The same conclusion is reached on the basis of the law of mass action. In the reaction $I_2 \rightleftarrows 2I$ the dissociation constant K_c is given by the expression—

$$K_c = \frac{(\text{concentration of iodine atoms})^2}{\text{concentration of iodine molecules}}.$$

Now if the pressure on the system be diminished, *i.e.* the volume increased, to such an extent that the concentration of the iodine atoms sinks to half its former value, the concentration of the iodine molecules would have simultaneously to sink to one-fourth their original value in order that K_c may remain constant. This means that the concentration of iodine molecules must decrease to a greater extent than the concentration of iodine atoms; in other words, some of them must cease to exist in the molecular form, *i.e.* the degree of dissociation is increased by diminishing the pressure.[1]

---

[1] The effect of pressure in the above case is therefore to alter the degree of dissociation. In such gaseous reactions the equilibrium constant as defined above

This alteration in the degree of dissociation with pressure is characteristic of all reactions of the second type.

Data obtained in the case of Nitrogen Peroxide.—The application of the vapour density method to the dissociation of N_2O_4 into NO_2 has yielded the following results. Temperature 49·7° C.

P.	Δ Observed and Referred to Air as Standard.	α.	K_p.
0·0 mm.	—	1·000	—
26·80 ,,	1·663	0·930	106
93·75 ,,	1·788	0·789	112
182·69 ,,	1·894	0·690	124
261·37 ,,	1·963	0·630	130
497·75 ,,	2·144	0·493	121

The value of K_p if theory is correct should be constant. This is roughly the case; the variations being irregular.

The Deacon Process of Chlorine Manufacture.—The reaction involved in this process is represented by the equation

$$O_2 + 4HCl \rightleftarrows 2H_2O + 2Cl_2.$$

A careful experimental investigation has been carried out by Lunge and Marmier (*Zeitsch. angewandte Chem.*, **105**, 1897). A mixture of hydrochloric acid gas and oxygen—the oxygen being sometimes replaced by air—was led over broken bricks which had been soaked in cupric chloride solution, then dried and heated to about 450° C. As a rule the gas mixture was originally dry, *i.e.* it contained no water vapour. The equilibrium was approached from one side only, *i.e.* the $HCl + O_2$ side, not from the chlorine-water-vapour side. The equilibrium equation in terms of partial pressures is—

$$\frac{p^2_{\epsilon H_2O} \times p^2_{\epsilon Cl_2}}{p_{\epsilon O_2} \times p^4_{\epsilon HCl}} = K_p,$$

or writing it as Haber does—

$$\frac{p^{\frac{1}{2}}_{\epsilon H_2O} \times p^{\frac{1}{2}}_{\epsilon Cl_2}}{p^{\frac{1}{4}}_{\epsilon O_2} \times p_{\epsilon HCl}} = K'_p \text{ where } K'_p = \sqrt[4]{K_p}.$$

is not altered numerically, because concentration terms depend directly upon (*i.e.* may be written in terms of) pressure terms. There is, however, an alternative mode of writing an equilibrium constant of a gaseous reaction which *does* vary with the pressure (*cf.* Vol. II., Chap. V.). Had the system been a liquid solution in which the pressure exerted upon the system bore no relation to the concentration terms of the substances reacting in the solution, then, as will be seen later (Vol. II., Chap. V.), in accordance with the principle of "mobile equilibrium" the equilibrium constant *itself* would alter numerically with alteration in externally applied pressure, provided the reaction is one which involves a volume change in the (liquid) system *as a whole*, no matter whether the reaction actually involves a "change in the number of molecules" or not, since volume changes in liquid systems are due to a variety of causes not effective in gaseous systems.

If a fraction x of each mole of HCl is decomposed when equilibrium is reached, this fraction will give rise to $\frac{x}{2}$ moles of chlorine, so that the ratio of the concentrations of these two constituents is, if v is the volume of the system—

$$\frac{\frac{x}{2v}}{\frac{1-x}{v}} = \frac{x}{2(1-x)} = \frac{p_{eCl_2}}{p_{eHCl}}.$$

Multiplying the equilibrium equation above and below by p_{eCl_2}, one obtains—

$$\frac{p_{eCl_2}}{p_{eHCl}} \cdot \frac{p^{\frac{1}{2}}_{eH_2O}}{p^{\frac{1}{2}}_{eCl_2}} \cdot \frac{1}{p^{\frac{1}{4}}_{eO_2}} = K'_p.$$

Now if we start with dry O_2 + HCl, we know from the stoicheiometric equation $O_2 + 4HCl = 2H_2O + 2Cl_2$, that just as much H_2O vapour will be formed as chlorine vapour, so that the partial pressures of these two constituents will always be identical at any stage in the reaction, and therefore identical at the equilibrium point. Hence the term—

$$\frac{p^{\frac{1}{2}}_{eH_2O}}{p^{\frac{1}{2}}_{eCl_2}} = 1,$$

and, therefore,

$$K'_p = \frac{x}{2(1-x)} \cdot \frac{1}{p^{\frac{1}{4}}_{eO_2}}.$$

This formula shows how relatively little the equilibrium point is influenced by the oxygen concentration or partial pressure, since it only occurs in the equation under a fourth root. Lunge and Marmier found that at the temperature at which they worked—in the region 400° to 500° C.—that the decomposition of HCl gas was large. When the initial mixture, for example, contained 8·5 per cent. HCl and 91·5 per cent. O_2, the fraction x of the initial HCl decomposed was 0·83, *i.e.* 83 per cent. A difficulty met with in the experiments was the decomposition of the catalyst, the cupric chloride, at the higher temperatures, thereby interfering with the calculated chlorine content. The catalyst certainly volatilises in the region of 470° C., and traces go over at even lower temperatures. In experiments carried out above 500° C., it is evident that some of the catalyst will be distilled into the cooler parts of the tube, and as the gas mixture passes over it in this region it will cause to some extent a change in the composition of the gas mixture (which has already reached equilibrium in the hottest portion) to another equilibrium state corresponding to the temperature of the cooler portion of the tube. Owing to this effect, it was found that the equilibrium constants, calculated from the results of experiments, carried out between 500° and

550° C., were not very different from those obtained at somewhat lower temperatures. This difficulty was got over later by Vogel von Falckenstein, who worked even up to 600° C., by using platinum chloride as catalyst at the higher temperature. The following table contains a few of the results of Lunge and Marmier at the temperature 430° C., starting with dry $HCl + O_2$.

Total Pressure in mm.	Initial Mixture.		x.	$p^{\frac{1}{4}}_{eO_2}$.	$K'_p = \frac{x}{2(1-x)} \cdot \frac{1}{p^{\frac{1}{4}}_{eO_2}}$.
	Per Cent. HCl.	Per Cent. O_2.			
737	8·5	91·6	0·83	0·97	2·51
733	15·7	84·3	0·81	0·96	2·74
736·5	16·3	83·7	0·83	0·95	2·57
737	21·0	79·0	0·82	0·93	2·45
729	34·1	65·9	0·81	0·88	2·42
735	51·1	48·9	0·77	0·81	2·07
729	67·4	32·6	0·58	0·71	1·00*
725	83·1	16·9	0·39	0·55	0·58*

The average value for the equilibrium constant K'_p at this temperature is 2·4 approximately. It will be observed that some values—those marked with *—are considerably less than this. This is easily accounted for if the reaction had not yet reached the equilibrium state in the experimental vessel. The important point to observe is that the discrepancy manifests itself when the HCl percentage in the mixture becomes large. One would expect this to be the case, because, in order that a heterogeneous catalyst such as pumice saturated with $CuCl_2$ may hasten the reaction, the reactant molecules must come into contact with the surface of the catalyst, a process which evidently depends on the actual extent of catalysing surface, and further, the greater the quantity of HCl to be decomposed, the longer the time required for every molecule to come into contact with the catalyst. In Marmier and Lunge's experiments with large quantities of HCl, the time presumably was not sufficient to allow the reaction to proceed to the equilibrium state, and hence the low values for the equilibrium constant. On using air instead of oxygen a similar discrepancy was observed when the HCl percentage was considerable, this being due to the dilution of the oxygen with the inert gas nitrogen, which also acted so as to slow down the rate at which equilibrium could be reached. To get the highest *percentage* of HCl decomposed, the conditions are small absolute quantity of HCl, and large absolute quantity of oxygen for a given quantity of catalyst at a given temperature. Thus in the first values given in the table the initial mixture contains only 8·5 per cent. HCl, and with it a large excess of O_2, with the result that equilibrium is rapidly attained, the fraction of the HCl decomposed being large, namely, 0·83. Under the experimental conditions realised in the experiments referred to, equilibrium is evidently reached until the initial mixture contains 35 per cent. or more of HCl, provided pure oxygen is present to make up the remaining percentage composition of the mixture. If oxygen, however, is replaced by air, then even at 26 per cent. HCl in the initial mixture, the equilibrium is not yet reached at the conclusion of the experiment, the constant being somewhat low, namely, 2·14. Also in this latter case the fraction of the HCl decomposed is only 0·71, while it was as high as 0·81-0·82 when pure oxygen was used in place of air. The values of K'_p vary, of course, with the temperature. Thus Marmier and Lunge found that at 480° the average value for K'_p was 2·0. The results in this case were much more concordant than in that previously quoted. This is no doubt due to the higher temperature, since it is known that the velocity of reactions increases markedly with the temperature. In a homogeneous reaction, *i.e.* one occurring in the gaseous state or in solution, the general rule is that a rise of 10° causes the velocity constant to be doubled or even trebled. The equilibrium point is therefore more rapidly reached at the higher temperature. It should be observed, however, that the numerical value of K'_p has diminished, with rise in temperature, and this means *ceteris paribus* that the quantity of chlorine formed from a given quantity of HCl is less than at lower temperatures. At the temperature 480° quite measurable quantities of chlorine were produced by decomposition of the catalyst. To obtain the optimum conditions for Cl_2 formation, one has therefore to take into account several factors such as prevention of decomposition of the catalyst, sufficient reaction velocity to reach equilibrium in reasonable time, and the temperature coefficient of the equilibrium constant itself. The results quoted will also serve to bring out how many factors go to determine the true realisation of the equilibrium point.

As already mentioned in the experiments referred to, the equilibrium point was only approached from one side. Vogel von Falckenstein (*Zeitsch. phys. Chem.*, **59**, 313, 1907; *Zeitsch. Elektrochem.*, **41**, 1906) has, however, carried out experiments in which it is approached from both sides, *i.e.* starting with a mixture of $Cl_2 + H_2O$ (vapour) as well as with a mixture of $HCl + O_2$. The following data were obtained, the "direct" process referring to those experiments in which the initial mixture consisted of $HCl + O_2$, the "reverse" process referring to the $Cl_2 + H_2O$ mixtures.

Temperature.	$K'_p = \frac{p_{eH_2O}^{\frac{1}{2}} \times p_{eCl_2}^{\frac{1}{2}}}{p_{eO_2}^{\frac{1}{4}} \times p_{eHCl}}$.		Mean K'_p.
	"Direct."	"Reverse."	
°C.			
450	2·31	2·22	2·26
600	0·98	1·04	1·01
650	0·804	0·789	0·796

(The values for 600° C. are not based upon so many experimental determinations as those at the other temperatures.) The agreement between the values of K'_p obtained by the different processes is very satisfactory.

THE "CONTACT" PROCESS OF SULPHURIC ACID MANUFACTURE.

The essential reaction involved here may be represented by—

$$2SO_2 + O_2 \rightleftarrows 2SO_3.$$

The equilibrium constant is—

$$\frac{p^2_{eSO_3}}{p^2_{eSO_2} \times p_{eO_2}} = K_p$$

or

$$\frac{p_{eSO_3}}{p_{eSO_2} \times p^{\frac{1}{2}}_{eO_2}} = K'_p.$$

The "contact" process derives its name from the fact that the $SO_2 + O_2$ gas mixture is passed over a solid catalyst—finely divided platinum—in contact with which the above reaction proceeds. A fairly full account of the literature will be found in Haber's *Thermodynamics of Technical Gas Reactions.* It is only necessary here to refer to some work of Bodenstein as illustrative of how such a reaction is investigated from the technical physico-chemical standpoint. Bodenstein's method consists in passing a mixture of SO_2 + air over hot platinised asbestos, contained in two quartz vessels. Combination takes place in the first vessel, thereby liberating a large amount of heat, which alters the temperature of the catalyst, and consequently tends to set up an equilibrium corresponding to this higher (unknown) temperature. The mixture when equilibrium is almost reached is transferred to the second vessel, and since the amount of transformation yet to be undergone is small, the heat effect is likewise small, so that the true equilibrium point corresponding to the temperature of the enclosure is realised. Temperature changes have a most marked effect upon this reaction. Some data will be given in the section dealing with the variation of K with the temperature. The advantage of using platinum in some form lies in the accelerating influence it exerts on the reaction, so that at temperatures below 500° equilibrium is reached sufficiently quickly to allow of the employment of rapid currents of gas, which is, of course, a highly important technical point where time is a factor which must always be considered. Without a catalyst the reaction is extremely slow below 500°, and if we raised the temperature sufficiently so as to allow of fairly rapid realisation of equilibrium, it would be found that the equilibrium point now corresponds to considerable dissociation of SO_3, *i.e.* only a relatively small amount of $SO_2 + O_2$ combines at high temperatures. It will be seen at once therefore how much the technical success of such a process depends upon the use of a good catalyst, which causes the reaction to go at a satisfactory rate under temperature conditions which are favourable to high percentage yield of the desired product. The above process, for example, was at first of no technical importance—compared with the older chamber process—owing to the want of a suitable catalyst, and later, even after platinum was in use for the purpose, the process again lost favour owing to some alteration of the platinum on continued use, which rendered it ineffective as a catalyst. This has been traced to the presence of impurities in the SO_2, which must be carefully eliminated before the gas mixture comes into contact with the catalyst, as otherwise a process known as "poisoning the catalyst" takes place. As a matter of fact, practically nothing is known as to what this poisoning really is—probably because we are still much in the dark regarding the mechanism of the catalysing effect itself. Recently it has been stated in connection with the SO_3 production that a certain rise in temperature will get over the difficulty of the poisoning without causing the formation of SO_3 to diminish too much.

VARIATION OF THE EQUILIBRIUM CONSTANT WITH TEMPERATURE.

Just as in the first-type gas reactions, so in those of the second-type, the numerical values of K_c and K_p or K'_p vary with the temperature. Some instances have already been given in connection with *the Deacon process*. A few more for the same reaction are here added for the sake of completeness.

Temperature.	K'_p Found.	Experimenter.	K'_p Calculated by Haber.
° C.			
352	4·02	G. N. Lewis	4·57
386	3·02	,,	3·40
419	2·35	,,	2·62
430	2·50	Lunge and Marmier	2·42
450	2·26	v. Falckenstein	2·10
480	2·0	Lunge and Marmier	1·73
600	1·02	v. Falckenstein	0·90
650	0·794	,,	0·728

The values of K'_p found were obtained by dynamic methods. As an indirect method one may call attention to the column of values headed K'_p calculated, which were obtained on a thermodynamical basis from certain energy relations applied to the separate reactions—

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

and

$$2H_2 + 2Cl_2 \rightleftarrows 4HCl$$

which on subtraction yield the Deacon equation. The ideas involved in this calculation cannot be understood until the reader has familiarised himself with the principles of Thermodynamics (Vol. II., Chaps. I. and II.). The temperature effect, as already pointed out, is of great technical significance. It is clear from the above data that the position of equilibrium becomes more favourable for the preparation of chlorine, the lower the temperature. In this process, therefore, the highest percentage transformation of HCl into chlorine would theoretically be obtained by working at as low a temperature as possible. A lower limit is, however, set to the temperature by the fact that with decrease in temperature the velocity of formation likewise diminishes. Technical work has shown that the best results are obtained if the reaction is carried out in the region of 400° C.

The data available in connection with the *contact process of sulphuric acid manufacture* are interesting as showing an exceedingly marked temperature influence. Haber (*l.c.*) gives the following table of K'_p values based on Bodenstein's data, the constant K'_p standing as before for—

$$\frac{p_{eSO_3}}{p_{eSO_2} \times p_{eO_2}^{\frac{1}{2}}}.$$

Temperature.	K'_p.
° C.	
528	31·3
579	13·8
627	5·54
680	3·24
727	1·86
789	0·956
832	0·627
897	0·358

At 450° Haber calculated from Knietsch's observations that K'_p was as much as 187·67, whilst it is only 0·358 at 897°. A large constant indicates large formation of SO_3, hence the lower the temperature the better the yield. It should be remembered that equilibrium values are always the maximum values for a given temperature which can possibly be obtained in any process, and hence the importance of studying these technical problems from the physico-chemical standpoint by means of which it is possible to say quantitatively—not empirically—when the limit of yield has been reached under given conditions. The condition of low temperature in the above case must, however, not be carried too far, for here again the question of time comes in, as it is of little benefit to know that a large yield may be obtained if expenditure of time be too great for its realisation.

EXPERIMENTAL METHODS OF DETERMINING EQUILIBRIA IN SECOND-TYPE GAS REACTIONS.

The methods may be divided as before into (1) static, (2) dynamic, (3) indirect (velocity constant measurements). We have already dealt with several instances of the first two methods. One point requires to be emphasised. Among static methods we find frequent use made of density determinations. This method is quite characteristic of second-type gas reactions, for it is only possible by this method to tell anything about the course of a reaction if the reaction itself involves a change in the total number of molecules and therefore gives rise to "abnormal" density values. To first-type gas reactions the density method is quite inapplicable. Dynamic methods on the whole are more generally in use, especially as many gas reactions are carried out at high temperatures, for which such methods are well suited. The experiments quoted in the case of the Deacon process and the contact sulphuric acid process are examples of dynamic methods. The indirect method of determination of equilibrium points by means of the velocity constants of the "direct" and "reverse" reaction is quite analogous to that employed in first-type gas reactions. As an example, the reader is referred to Nernst and Jellinek's determination of the equilibrium constant of the reaction—

$$N_2 + O_2 \rightleftarrows 2NO$$

(*Zeitsch. anorg. Chem.*, **49**, 229, 1906),

which is of great technical importance in connection with the problem of the fixation of atmospheric nitrogen.

THE EFFECT OF ADDING VARIOUS SUBSTANCES TO SYSTEMS ALREADY IN EQUILIBRIUM.

Two important cases arise in this connection:—

First, what is the effect of adding an indifferent gas (*i.e.* one which does not react chemically) to a gas system already in equilibrium, (*a*) the addition of the indifferent gas being made at constant volume, (*b*) the addition causing an increase in volume at constant pressure?

Secondly, what is the effect of adding one of the components of the reaction to a system already in equilibrium, (*a*) the volume being kept constant, (*b*) the volume being allowed to increase?

As regards the first question, both types of gas reaction may be considered simultaneously. On adding an indifferent gas to a gaseous system representing, say, a dissociation equilibrium ($N_2O_4 \rightleftarrows 2NO_2$ or $2HI \leftrightarrows H_2 + I_2$) and keeping *the volume constant*, it is evident that the total pressure must increase. *Experience has shown that the percentage dissociation or decomposition is not altered thereby.* This is in agreement with what one would expect on the basis of Dalton's Law, for by this law the presence of a foreign inert gas does not influence the partial pressures exerted by the reacting components. This holds equally well whether the reaction itself involves a change in the total number of molecules or not. This behaviour must not be confused with the effect of increased pressure on second-type gas reactions, which we have already discussed, and in which we found that increasing the pressure or decreasing the volume caused a certain amount of recombination to take place. In the case of *compression* simply, the point to be noticed is that the increase in pressure was carried out in such a way that the partial pressure of *each* component was increased, while in the case of the addition of the inert gas the *total* pressure is increased (at constant volume) while each partial pressure remains unaltered. Now we come to the second part of the first question, *viz.* what happens if we add an indifferent gas to a gas system in equilibrium in such a way that the volume of the system increases while the *total* pressure remains the same? Here we have evidently diluted the system. Now it has already been seen that in first-type gas reactions the equilibrium is unaffected by volume (*e.g.* HI, H_2, I_2), and therefore there is no change in the fraction dissociated in such a case, though, of course, the absolute values of the partial pressures have fallen since the same mass of each component is now distributed throughout a larger volume. In the case of second-type reactions the result is different. The increase of volume at constant pressure causes, as we have seen, an increase in the dissociation products. By the addition of the indifferent gas we have—just as in first-type reactions—decreased the partial pressure of each reacting component, and in second-type reactions the fraction dissociated depends on the total pressure exerted by the components, which is now less than before although the total pressure of the system remains constant. Hence the effect of dilution is to cause dissociation of second-type reactions to *increase*.

We may summarise the above effects as follows:—

Addition of inert gas.	If volume is kept constant: no chemical change in both first- and second-type reactions. If volume increases: no chemical change in first-type reactions. Increase in dissociation (the dissociation *constant* remaining the same, of course) in the second-type reactions.[1]

EFFECT OF ADDING ONE OF THE REACTING CONSTITUENTS, THE SYSTEM BEING KEPT AT CONSTANT VOLUME.

DIVISION A.—FIRST-TYPE REACTIONS.

These must be further subdivided into: (1) Reactions in which *one* kind of chemical substance gives rise to one other kind; (2) one kind of substance yields two or more different kinds; (3) two or more kinds give rise to two or more different kinds still. It will be convenient to work with concrete examples.

Subdivision (1).—No examples are known. Isomeric changes would belong to this group, but none are known in gases.[2] Let us take the hypothetical case $1A \rightleftarrows 1B$ for which the equilibrium constant is $\frac{C_{eB}}{C_{eA}}$, what is the effect of adding some B, keeping the volume constant? The pressure obviously will be increased. A simple way of finding out what is likely to happen in all these cases where some constituent is added, is to imagine the state which is reached "momentarily" on adding the gas in question. That is, we imagine the gas added so quickly (yet without any heat effects) that the rest of the system remains as it was during this moment even if it should ultimately alter. The method is perhaps a little artificial, but it allows one to predict what will happen assuming the applicability of the law of mass action. If experience in all cases is in agreement with the prediction, it obviously affords very conclusive proof of the validity of the law.

---

[1] Dissociation is a particular kind of a second-type reaction. In general one may say that diluting a second-type reaction—the total pressure being kept constant—causes the reaction to go toward the side of the equation which contains the greater number of molecules, *i.e.* in the reaction, $1A + 2B \rightleftarrows 3C + 4D$, the effect of dilution in the above manner will be to cause an increase in C and D.

[2] Perhaps the active modification of nitrogen, recently discovered by Strutt on passing electric sparks through nitrogen, may belong to this group, but nothing is known regarding this point.

Let us consider now what happens on increasing the concentration of B by adding it to the system at constant volume. "Momentarily" we have A at concentration C_{eA} and B at concentration C'_B, and the expression $\frac{C'_B}{C_{eA}}$ is therefore greater than before, and hence if we are to have a constant at all, it is clear that a chemical change must take place in the system whereby the concentration of B decreases and A increases, *i.e.* the reaction goes thus, B → A.

Similarly, had we added excess of A, the reaction would have gone in the opposite direction. The effect therefore of adding excess of either of the components in this case is to cause part of this excess to be used up in the production of some of the other component. The net effect therefore is that the *concentration* of *both* components is increased. In spite of this, however, the *fraction decomposed* of A, say, is not altered from the former state, because the ratio of the concentrations of A and B must remain constant, and this can be written in the form—

$$\frac{\frac{x}{v}}{\frac{1-x}{v}}$$

(where x is the fraction of one mole of A which disappears to give rise to B), an expression which is obviously independent of the dilution v (and therefore of the concentration which is the reciprocal of v) since this quantity v cancels out, leaving $\frac{x}{1-x}$ constant and therefore x constant.

Subdivision (2).—An example is the familiar reaction $2HI \rightleftarrows H_2 + I_2$. What is the effect of adding excess of H_2 to this system when in equilibrium, keeping the volume constant? According to the law of mass action—

$$\frac{p_{eH_2} \times p_{eI_2}}{p^2_{eHI}}$$

is constant (at a given temperature). "Momentarily" we shall have the pressure of the H_2 increased, say, to p'_{H_2}, and the expression—

$$\frac{p'_{H_2} \times p_{eI_2}}{p^2_{eHI}}$$

would now be too large, so that in order that the equilibrium constant may retain its original value, part of the H_2 and I_2 must unite to give some HI, *i.e.* the decomposition of HI is thrown back. Evidently just as much HI will thus be formed as corresponds to I_2 disappearing in the process. Analogous results would have been obtained had we added excess I_2 vapour instead of H_2. We may therefore generalise by saying that the degree of decomposition of HI is diminished by the addition at constant volume of either of the products of decomposition. By preferentially adding only one of the products of decomposition we bring about a state of things which might be called "an asymmetrically decomposed system," because the products are not present in equivalent quantities. Such an asymmetric state never occurs as a result of spontaneous action, but can be brought about in the manner above described. When we speak of "the degree of decomposition" in such a case as the above, it is not quite the same as the ordinary decomposition into equivalent amounts of H_2 and I_2. By adding H_2 we have decreased I_2 and accordingly increased the HI. Hence the ratio $\frac{I_2}{HI}$ has decreased, and if we add a large amount of H_2 we can make the I_2 almost vanish. It is *this* degree of dissociation which decreases, *i.e.* dissociation with respect to the constituent which has *not* been artificially increased. This does not contradict the conclusion to which we came earlier, namely, that the degree of dissociation of any first-type reaction is independent of the volume or concentration of the system, for then we were only thinking of symmetrical decomposition into equivalent amounts of H_2 and I_2. This can be seen at once if we imagine the effect which will be produced if we add H_2 and I_2 simultaneously in equivalent amounts. In order to keep the equilibrium constant the same, H_2 and I_2 will combine to a certain extent, the uncombined portions necessarily remaining in equivalent quantities. The result of such a proceeding will be to increase the *concentration* of all the constituents, namely, the HI, H_2, and I_2, but the *degree* of decomposition will be absolutely unaltered, for evidently we could have arrived at the same state not by adding H_2 and I_2 in equivalent quantities, but by simply compressing the system. Clearly, the same reasoning applies if we add HI to the original system. In this case the expression—

$$\frac{p_{eH_2} \times p_{eI_2}}{p^2_{HI}}$$

would momentarily be too small, and hence some of the HI will decompose, but this it can only do symmetrically into equivalent H_2 and I_2, so that, although each concentration or partial pressure term is increased, the fraction decomposed is unaltered. If, however, we make the composition of the system asymmetric by preferential addition of one of the products of decomposition as already stated, the degree of dissociation with respect to the other product is decreased. In this type of reaction the student must be careful not to make the statement that the addition of any constituent will alter the degree of decomposition, for, of course, HI itself is a constituent, and we have seen that the addition of this does not alter the degree of decomposition. The whole matter may be simply put thus: if symmetrical change is caused in the system at constant volume (by addition of HI), the degree of decomposition remains unchanged; if the system becomes asymmetric by the addition of one product of decomposition, the degree of decomposition with respect to the other product is decreased. The difference between subdivisions (1) and (2) is now clear, because under no circumstances can we make the reaction of subdivision (1) asymmetric. The student must also bear in mind that we are discussing first-type reactions only.

Subdivision (3).—This includes reactions such as that represented by the equation—

$$A + B \rightleftarrows C + D$$

or more generally—

$$n_1A + n_2B \rightleftarrows n_3C + n_4D$$

where

$$n_1 + n_2 = n_3 + n_4$$

and the substances A, B, C, and D are all different. Each substance can be added in turn, so that concentration asymmetry can be introduced into the system from either side of the equation. This distinguishes such reactions from that of subdivision (2), in which asymmetry could only be brought about from one side (*i.e.* in the hydriodic acid decomposition by addition of either H_2 or I_2). As an illustration we may consider the water gas reaction—

$$CO_2 + H_2 \rightleftarrows H_2O + CO$$

for which the equilibrium constant K_c is—

$$\frac{C_{cH_2O} \times C_{cCO}}{C_{cCO_2} \times C_{cH_2}}.$$

If one adds at constant volume *either* water vapour or carbon monoxide, formation of some $CO_2 + H_2$ results. Similarly, addition of either carbon dioxide or hydrogen causes the production of some $H_2O + CO$. We can no longer speak of degree of decomposition in such a case, since all the substances are different, and a single substance does not of itself produce any other substance. In so far as investigation has gone in gaseous reactions, no exception has been met with as regards the law of mass action.

DIVISION B.—SECOND-TYPE GAS REACTIONS.

We have now to consider second-type gas reactions as regards the effect of adding components to a system already in equilibrium, the system being kept as before *at constant volume.* It is not necessary to make any subdivisions here. It will be remembered that these reactions are characterised by the fact that the degree of dissociation—when the reaction happens to be simply a dissociation such as $N_2O_4 \rightarrow 2NO_2$—alters with the dilution of the system. The following statement holds good: If to a second-type reaction system in equilibrium we add at constant volume *any* one of the constituents the degree of dissociation is thereby altered. This happens whether the dissociation is made symmetrical or not. Consider the simple type of reaction represented by the dissociation of molecular iodine into atomic iodine, according to the equation $I_2 \rightleftarrows 2I$. The equilibrium constant—

$$K_c = \frac{C^2_{eI}}{C_{eI_2}}.$$

If we could imagine iodine *atoms* added, the pressure rises since the volume is kept constant, and consequently we get formation of I_2 molecules, but, for reasons given when discussing the effect of external pressure in such a case, not only is the absolute concentration of each constituent increased, but at the same time the degree of dissociation of the iodine molecules is decreased. The degree of dissociation would be simply—

$$\frac{\text{concentration of I}}{\text{concentration of } I_2}$$

and it is clear that this cannot be constant, since it is the expression—

$$\frac{(\text{concentration of iodine atoms})^2}{\text{concentration of iodine molecules}}$$

which remains constant. The degree of dissociation, as well as the absolute concentration terms of each constituent is likewise altered by addition of molecular iodine—this being the only practical addition we can make.

Further, take the case in which two different products are formed by dissociation, *e.g.* the dissociation of phosphorus pentachloride, $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The temperature is supposed to be such that all the constituents are gaseous. The equilibrium constant is—

$$K_c = \frac{C_{ePCl_3} \times C_{eCl_2}}{C_{ePCl_5}} \text{ or } K_p = \frac{p_{ePCl_3} \times p_{eCl_2}}{p_{ePCl_5}}.$$

Suppose some chlorine is added, the "momentary" state is evidently not one of equilibrium, the above expression being now greater than before. Partial combination of PCl_3 and Cl_2 occurs, giving rise to some PCl_5. The system is also at a higher pressure now than it was previous to the addition, and hence the degree of dissociation of the PCl_5 is less. The addition of one of the products of dissociation therefore throws back the degree of dissociation, just as in first-type reactions[1] at constant volume. Also if some PCl_5 be added, the above expression is momentarily too small, and hence some of the PCl_5 added dissociates. The total pressure (due to the sum of the partial pressures) has increased, and therefore the degree of dissociation of PCl_5 is once more decreased. An exactly similar effect would of course have been produced by adding $PCl_3 + Cl_2$ in equivalent quantities. In first-type reactions, however (HI, H_2, I_2), the degree of decomposition of the HI is not affected by addition of HI, although of course the absolute concentration value of each constituent is increased if the volume be kept constant. For second-type reactions ("dissociations") it is therefore quite correct to say that addition of *any* constituent at constant volume will decrease the degree of dissociation; for first-type reactions it is only by adding *certain* constituents, so as to set up a state of "asymmetric decomposition," that the degree of decomposition is thrown back (with respect to the constituent not artificially increased).

---

[1] The system being thereby made "asymmetric".

Further, let us consider the Deacon process—

$$O_2 + 4HCl \rightleftarrows 2Cl_2 + 2H_2O$$

which gives a constant—

$$K_p = \frac{p^2_{eCl_2} \times p^2_{eH_2O}}{p_{eO_2} \times p^4_{eHCl}}.$$

This might be considered as a second-type reaction analogue of the water-gas reaction $CO_2 + H_2 \rightleftarrows H_2O + CO$. The behaviour of the Deacon reaction resembles the water-gas reaction in that the addition of any *one* of the constituents causes a general increase in the concentration of all the constituents, in order to keep K_p constant, the volume having been kept unchanged. There is the following marked difference, however. If one adds in the Deacon reaction some $Cl_2 + H_2O$ in the correct stoicheiometric quantities required by the reaction equation (one mole of each), some $HCl + O_2$ will be produced, *i.e.* the absolute values of the concentrations are increased, and since the addition has been made at constant volume, the pressure has risen, but the *ratios* of the numerator terms to the denominator terms must not remain the same as before, for if this were the case it is obvious that raising *some* of them to different powers as they appear in the equilibrium equation would not when thus raised yield the same value for K. In the water-gas reaction, however, the addition of $H_2O + CO$ in stoicheiometric quantities leaves the equation in such a state that the ratios of the numerator terms to those of the denominator, *i.e.*—

$$\frac{p_{H_2O}}{p_{CO_2}} \text{ or } \frac{p_{CO}}{p_{H_2}} \text{ or } \frac{p_{H_2O}}{p_{H_2}}$$

are just the same as they have been previous to the addition. The absolute values of the concentration terms are, of course, increased.

We may now pass on to the final part of the problem, namely:—

EFFECTS PRODUCED IN FIRST- AND SECOND-TYPE GAS REACTIONS BY THE ADDITION OF DECOMPOSITION PRODUCTS AT CONSTANT PARTIAL PRESSURE OF THE ADDED CONSTITUENT.

The volume of the system evidently increases to a greater or less extent under these conditions. The case is scarcely so important as the preceding, but it is, nevertheless, of interest to see what behaviour the law of mass action predicts. We shall not trouble to treat the two types of reaction separately. Instead, we shall simply consider one or two special cases.

(i) The reaction involves the dissociation of one kind of molecule into two new kinds, *e.g.* the dissociation of phosphorus pentachloride, $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The condition for equilibrium is that—

$$\frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v}} = \text{constant, K,}$$

where x is the mass of chlorine or phosphorus trichloride (in moles) present in the volume v (liters), and $(1 - x)$ is the mass of phosphorus pentachloride. x is therefore the degree of dissociation or fraction of one mole of PCl_5 dissociated. Now suppose nv liters of Cl_2 or PCl_3 are added at the same partial pressure as that at which these substances exist in the mixture. Consider the "momentary" state. The volume increases to $(n + 1)v$ liters while the total pressure of the system remains the same as before, since the Cl_2 or PCl_3 has been added at its original partial pressure. The original partial pressure of Cl_2 or PCl_3 corresponded to a concentration of x moles in v liters. By adding nv liters under the same conditions we have added nx moles of chlorine (say), so that the total mass of chlorine is now $(n + 1)x$ moles, and this is "momentarily" distributed throughout a volume $(n + 1)v$, so that its concentration is $\frac{(n + 1)x}{(n + 1)v}$.

During the "momentary" state therefore we have the following concentration relations:—

$$\frac{\frac{x}{(n+1)v} \cdot \frac{(n+1)x}{(n+1)v}}{\frac{1-x}{(n+1)v}}$$

which is evidently identical with the former expression—

$$\frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v}}.$$

In other words, the "momentary" state in this case turns out to be an equilibrium state. Hence the addition of either Cl_2 or PCl_3 *at the same partial pressure as that already existing in the equilibrium mixture,* so that the system increases in volume while the total pressure likewise alters, has no influence on the degree of dissociation of the PCl_5. This conclusion should be compared with that when Cl_2 or PCl_3 is added, the system being kept at constant volume, in which case the degree of dissociation is thrown back.

(ii) The reaction involves a dissociation wherein *one* molecule of a substance gives rise to *three* molecules, *two* of which are identical, *e.g.* the dissociation of ammonium carbamate into ammonia and carbon dioxide—

$$NH_2COONH_4 \rightleftarrows 2NH_3 + CO_2.$$

The equilibrium constant is given by—

$$K = \frac{\left(\frac{x}{v}\right)^2 \times \frac{x}{v}}{\frac{1 - x}{v}}$$

where x is the fraction dissociated of one mole of NH_2COONH_4. First of all, suppose we add nv liters of CO_2 at the same partial pressure as that already possessed by the CO_2 in the equilibrium mixture. The volume increases to $(n + 1)v$ liters. The total mass of CO_2 is $(n + 1)x$ moles and the above expression becomes—

$$\frac{\left\{\frac{x}{(n + 1)v}\right\}^2 \times \frac{(n + 1)x}{(n + 1)v}}{\frac{1 - x}{(n + 1)v}}, \text{ which is equal to } \frac{\frac{x^2}{(n + 1)v^2} \times \frac{x}{v}}{\frac{1 - x}{v}}.$$

And this is no longer equal to the original mass action expression. The numerator has decreased, and in order that the constant K may remain as such, the numerator terms, that is, the dissociation products, must increase. *Hence the effect of adding the* CO_2 *under the above conditions is to cause the carbamate to dissociate further.**

Now consider what happens if NH_3 be added instead of CO_2. Suppose nv liters of NH_3 added at the partial pressure already obtaining in the equilibrium mixture. The mass of NH_3 is now $(n + 1)x$ in the volume $(n + 1)v$, and hence the mass action expression is at the momentary state—

$$\frac{\left\{\frac{(n + 1)x}{(n + 1)v}\right\}^2 \times \frac{x}{(n + 1)v}}{\frac{1 - x}{(n + 1)v}} = \frac{\left(\frac{x}{v}\right)^2 \times \frac{x}{v}}{\frac{1 - x}{v}}$$

which is identical with the original value. Hence the degree of dissociation of the carbamate is in this instance unchanged. If $NH_3 + CO_2$

were added, each at the correct partial pressure, it will be seen on setting up the equation that the degree of dissociation of the carbamate will be thrown back.

(iii) Finally consider the reaction $2HI \rightleftarrows H_2 + I_2$. The condition for equilibrium is that—

$$\frac{\frac{x}{v} \times \frac{x}{v}}{\frac{1-x}{v}} \text{ or } \frac{x^2}{(1-x)^2}$$

shall be constant.

If *nv* liters of hydrogen be added at the correct partial pressure the momentary state will be represented by—

$$\frac{\frac{(n+1)x}{(n+1)v} \times \frac{x}{(n+1)v}}{\left\{\frac{1-x}{(n+1)v}\right\}^2} \text{ or } \frac{(n+1)x^2}{(1-x)^2}.$$

The numerator is now too large, and in order that the equilibrium constant may retain its original value the decomposition of the HI must be thrown back.

The behaviour of systems which undergo volume increase by the addition of one or more of the reacting constituents differs from case to case, but it can in general be foretold by applying the law of mass action.

It may be pointed out that writing the volume increase as the sum of the original mixture and added gas only holds in certain cases when equilibrium is finally reached. If we take those cases in which no change is produced in the degree of dissociation by the addition, then the equilibrium volume is actually the "momentary" volume. In other cases, however, in which the addition causes the dissociation to alter, it will be found that finally, *i.e.* at the equilibrium state, the volume is not simply the sum of the original plus added gas, but has some other value. If the degree of dissociation is thrown back there will be an actual disappearance of molecules, and the final volume will be less than the momentary volume in order that the total pressure may be constant. The opposite effect occurs when the dissociation has been increased by the addition. The device of the "momentary" state is of great use, however, in telling us qualitatively at any rate what will happen.

CHAPTER IV.

Chemical equilibrium in homogeneous systems (*continued*)—Liquid mixtures—Solutions—Properties of solutions.

THE systems to be considered may be divided into (1) liquid mixtures and (2) solutions. The terms are not employed very rigidly, the term solution being not infrequently applied to include liquid mixtures as well. The distinction, such as it is, refers to the relative quantity in which the various constituents of the system coexist. The term "liquid mixture" applies strictly to a homogeneous liquid system in which no single constituent is present in very large excess compared to the other constituents. The separate constituents are at the same time liquids. A (liquid) solution, on the other hand, is a liquid system in which one liquid—called the solvent—is present in large excess. The constituents dissolved in the solvent are known as "solutes". Solutions may be produced by dissolving solids, liquids, or gases in a given solvent. The latter functions as the medium in which the reaction takes place and may in certain cases take a definite part in the reaction. In other cases—and these are the most frequently occurring—no definite *rôle* can be assigned to it, *i.e.* it does not appear in the stoicheiometric equation representing the reaction, but apparently functions as an inert medium. The properties of solutions and the types of equilibria which are found vary much according to the chemical nature of the solvent, for this determines to a certain extent the nature of the individuals produced by dissolving a given solute.

It has already been shown that the law of mass action is a satisfactory guide as far as gaseous reactions are concerned. Reaction there takes place between molecules, between atoms, and between molecules and atoms. We did not have to deal with electrical effects.[1] In liquid systems, however, besides reactions between molecules similar to gaseous molecules, we sometimes find instances of reactions between electrically charged particles called "*ions*," which are atoms or radicles carrying electricity proportionate to their valency. Ions occur most frequently in aqueous solutions of substances known as "*electrolytes*," notably inorganic acids, salts, and some bases, *e.g.* solutions of caustic potash, hydrochloric acid, sodium chloride, etc. Ions also occur, though to a much less extent, in solutions of similar substances in acetone, methyl alcohol, ethyl alcohol, and in a few other organic solvents. Solutions in which liquids such as hydrocarbons (aliphatic and aromatic) act as solvents do not contain ions, or at most only a very few. Ions may be of two kinds, according to the sign of the electrical charge carried, namely, positive ions or cations and negative ions or anions. Solutions are, however, in all cases electrically neutral, as the anions and cations are always present in equivalent numbers.

---

[1] In the case of a gas which has been ionised by electrical discharge, or by the rays of radio-active substances mentioned in Chapter I., the rate of combination of electrified particles to yield a neutral gas appears to follow the mass action principle.

In addition to reactions between ions, we also find reactions occurring between (uncharged) molecules and ions. As a matter of fact, when ions are produced some molecules are likewise present, though in certain cases to a very small extent. Reactions in liquids may therefore be more complicated in nature than those which occur in gases. The law of mass action has, however, been applied to equilibrium in liquid systems with considerable success. In such cases we take as a measure of the active mass of a constituent its concentration reckoned in moles per liter of solution, whether the constituent is electrically charged or not.

For the purpose of systematising our study we may classify reactions into (1) reactions in liquid mixtures, and (2) reactions in solutions. Reactions in solution are those which, as already mentioned, take place in a suitable liquid medium—the solvent—which is present in large excess, but which does not take part *apparently* in the reaction. Though the equilibrium relations can be satisfactorily studied in many cases without taking the solvent into account except as an inert diluent, it would be rash to suppose that it actually plays no part, since the nature of the solvent frequently determines the nature of the dissolved particles of solute. In certain solvents the solute may give rise to ions, that is to say, the solute may suffer "electrolytic dissociation"; in others, even the same solute will be quite unable to ionise. In other cases still, a definite stoicheiometric part is played by the solvent as in the hydrolysis of salts in aqueous solutions. For convenience we shall consider equilibria involving ions in the next chapter, under the head of the "electrolytic dissociation theory," since this forms by far the most important branch of reactions in liquid systems.

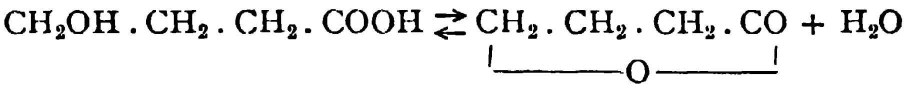
1. Liquid Mixtures

Our present purpose is to see how far the law of mass action has been established for reactions between uncharged liquid molecules when these are not suspended in a solvent—inert or otherwise—but are simply spatially distributed in the manner peculiar to the liquid state.

As an example, we may consider the *change of ammonium thiocyanate into thiourea*, according to the equation—

$$NH_4CNS \rightleftarrows (NH_2)_2CS.$$

At ordinary temperatures both these substances are solids and each may be kept for an indefinite time without alteration. This is due to the fact that reactions in the solid state are always very slow. The change, however, has been studied in the liquid state by working at a higher temperature, 152° to 153° C., at which the system is in a state of fusion. Experiments have been carried out by J. Waddell (*Journ. Phys. Chem.*, **2**, 523, 1898), beginning with each substance in turn. The same equilibrium point corresponding to the above temperature was reached from both sides, the equilibrium mixture being 21·2 per cent. thiocyanate and 78·8 per cent. thiourea. A little doubt exists regarding the numerical accuracy of the above numbers owing to the fact that the materials were not absolutely pure.[1] The results show quite definitely, however, that an equilibrium point is actually reached. The difficulty of applying the law of mass action, however, in such a case lies in what one means by "concentration" and whether concentration (moles per liter) is a true measure of the active mass. A similar type of reaction is met with in the conversion of γ-hydroxybutric acid into γ-butyrolactone.[2]



$$CH_2OH\,.\,CH_2\,.\,CH_2\,.\,COOH \rightleftarrows \underbrace{CH_2\,.\,CH_2\,.\,CH_2\,.\,CO}_{O} + H_2O$$

investigated by P. Henry (*Zeitsch. physik. Chem.*, **10**, 98, 1892). Starting with 18·23 moles of the acid, it was found that equilibrium was reached when 13·28 moles had been transformed. There were therefore 4·95 moles of acid left. If the volume of the system is v liters, the concentration of acid at the equilibrium point is $\frac{4{\cdot}95}{v}$, that of lactone or water being $\frac{13{\cdot}28}{v}$, and the equilibrium constant $K = \frac{(13{\cdot}28)^2}{4{\cdot}95v}$. The experiments being carried out for a different purpose, Henry did not investigate the constant further. Fairly good velocity constants were obtained, however, and this is evidence that mass action is effective in bringing about the state of equilibrium.

The most thoroughly investigated case of equilibrium in a liquid mixture is that furnished by the *action of ethyl alcohol upon acetic acid*, according to the equation—

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

This reaction was studied by M. Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.*, **65**, **66**, 1862; **68**, 1863). The reaction goes slowly at ordinary temperatures, several days being required to reach the equilibrium point. It may, however, be reached in a few hours by sealing up the mixture of alcohol and acid in a glass tube and heating to about 100° C. The stage reached after any interval of time may be determined in this case by titrating the acetic acid present. This method is only allowable if the reaction is a very slow one, no measurable change in the state of the system, *i.e.* no fresh acid being produced, during the time taken for titration. In reactions which go more rapidly this method would be quite inapplicable; in such cases we must have recourse to the measurement of some physical property which can be made without altering the relative concentrations of any of the reacting substances. Berthelot and St. Gilles established the fact that the same equilibrium point is reached whether we start with alcohol and acid or with ethyl acetate and water. Employing one mole of each substance to start with, on allowing the respective pairs to react the same equilibrium point was reached in both cases, namely: $\frac{1}{3}$ mole acetic acid, $\frac{1}{3}$ mole ethyl alcohol, $\frac{2}{3}$ mole ethyl acetate, $\frac{2}{3}$ mole water. After the lapse of several years these ratios were found to be absolutely unchanged.

---

[1] See Mellor, *Statics and Dynamics*, p. 86.

[2] *Ibid.*, p. 82.

Let us now calculate the equilibrium constant for the above case. Suppose the volume of the system is v liters.

Equilibrium concentrations are:—

Acetic acid.	Ethyl alcohol.	Ethyl acetate.	Water.
$\frac{\frac{1}{3}}{v}$	$\frac{\frac{1}{3}}{v}$	$\frac{\frac{2}{3}}{v}$	$\frac{\frac{2}{3}}{v}$

$$\text{The equilibrium constant K} = \frac{C_{e\,\text{ester}} \times C_{e\,H_2O}}{C_{e\,\text{acetic}} \times C_{e\,\text{alcohol}}}$$
$$= \frac{(\frac{2}{3})^2}{(\frac{1}{3})^2} = 4.$$

It will be observed that the above reaction is one which does not involve a change in the number of molecules. The v term, therefore, vanishes. If the system were gaseous, change of pressure would have no effect upon the numerical value of the *degree* of decomposition of the acid or alcohol.

Even in a reaction such as the above, however, where there is no change in the *number* of reacting molecules there may be slight volume change owing to the different cohesion attractions or repulsions possessed by the molecules of the different species produced in the liquid state. If there is absolutely no change in volume as the reaction proceeds, change in external pressure can have no effect upon the value of the constant K. If, on the other hand, there is a slight volume change of the system as a whole, produced as a result of the reaction, then the value of K will be slightly affected by alteration in the external pressure. Usually the effect is so very small that it may be neglected; theoretically, however, it is present, being analogous to the change of K with temperature, both effects being instances of the principle of "mobile equilibrium".

Returning to the equilibrium equation, it will be seen that it may be put in a somewhat more general form by supposing that the initial mixture consists of 1 mole of acetic acid, *m* moles ethyl alcohol, and that equilibrium is reached when x moles of ethyl acetate (or water) are formed. Then

$$K = \frac{x^2}{(1 - x)(m - x)}.$$

Employing the numerical value of K obtained from the experiment already quoted, we can calculate x for any other case and compare it with the value given by experiment. The following table (recalculated) is due to van 't Hoff (*Ber.*, **10**, 669, 1877), the values being based upon Berthelot and St. Gilles' data.

Initial Quantity of Acetic Acid.	Initial Quantity of Alcohol.	x Calculated.	x Found.
1 mole	0·05 mole	0·049 mole	0·05 mole
"	0·18 "	0·171 "	0·171 "
"	0·33 "	0·301 "	0·293 "
"	0·50 "	0·423 "	0·414 "
"	1·00 "	0·667 "	0·667[1] "
"	2·00 "	0·850 "	0·858 "
"	8·00 "	0·970 "	0·966 "

An examination of the data indicates that the law is approximately obeyed. This agreement, however, is to a certain extent illusory. In the first place the experimental values in the above case are barely accurate enough to allow us to distinguish between an apparent and a real agreement. In the second place, a much more fundamental point must be taken into consideration. It will be shown in the concluding section of this chapter that it is only legitimate to apply the law of mass action to a dilute system, that is one in which the concentration of the participating substances is low. This is most conveniently realised by employing a large quantity of an inert solvent. In general when the concentrations of all the substances in a reaction mixture are large, the law of mass action cannot be expected to hold good. Thus in regard to the above reaction, in a particular case in which there were a moles of ester already present in an equimolecular mixture of alcohol and acid the equilibrium values of x and the corresponding values of K are as follows:—

a.	x experimental.	K.
0·05	0·639	3·4
0·43	0·589	3·6
1·6	0·521	4·8

The values of K in this case show a decided trend, not to be explained on the ground of experimental error.

Another illustration of mass action equilibrium in liquid mixtures is afforded by the action of amylene upon organic acids to form amyl esters (Nernst and Hohmann, *Zeitsch. physikal. Chem.*, **11**, 352, 1893). Again we find an approximate constancy in the value of K but the experimental error appears to be somewhat large.

---

[1] **This result was used for the calculation of K in the first instance, hence the agreement in the last two columns is necessarily exact.**

The Berthelot-St. Gilles' reaction has recently been reinvestigated by Jones and Lapworth (*Trans. C. S.*, **99**, 1427, 1911), using hydrochloric acid as the catalysing agent to hasten the course of the reaction. Their results are very important from the standpoint of the mechanism of such catalysis, for they consider they have succeeded in showing that part of the HCl unites with part of the H_2O, thereby virtually removing part of the latter from active participation in the Berthelot reaction, with the result that calculations made of the equilibrium constant on the basis that all the water present is *active* lead to a series of different values for K—"apparent" values denoted by the symbol ψ—according to the amount of HCl in the system. Berthelot and St. Gilles did not employ a catalyst. The following account of Jones and Lapworth's experiments is given in their own words.

$$\text{The equilibrium constant } K = \frac{[H_2O][CH_3 . CO_2 . C_2H_5]}{[C_2H_5 . OH][CH_3 . CO_2H]}$$

is known to be approximately 4 for the homogeneous liquid system over a very wide range of temperature, its value being but slightly affected by the addition of small quantities of catalysts, by alterations in the relative amounts of the constituents, or by the use of various indifferent solvent media.

Whilst the activity of hydrogen chloride in alcohol is greatly diminished by small amounts of water, it is but imperceptibly affected by acetic acid or by ethyl acetate; hence, if the variations in the availability of hydrogen chloride are, in fact, due to combination of the latter with water, then hydrogen chloride, when passed into an equilibrium mixture of water, ethyl acetate, alcohol, and acetic acid, should unite almost exclusively with the water when the latter is there in considerable quantity. The experience of Berthelot and Péan de St. Gilles with indifferent solvents would lead to the conclusion that the value of K, corrected for the quantities of the four constituents removed by the hydrogen chloride and rendered inert, would still remain nearly constant. The present paper, *i.e.* that of Lapworth and Jones, describes measurements of this kind, which show that as the ratio of the amount of water existing in equilibrium to the amount of hydrogen chloride falls, the value of ψ (the apparent value of K calculated on the assumption that the water in the system is entirely in the free state) rises from 4 to 8 at least, indicating clearly that some of the water present combines with the hydrogen chloride. Further, assuming that this apparent variation in the "constant" is, as suggested, due to hydrate formation, it may be calculated that, roughly, two molecules of water associate with each molecule of hydrogen chloride present, although the existence of higher hydrates in a partly dissociated condition is not excluded.

The procedure in each of the experiments was as follows. Ordinary test-tubes were subjected to the action of a current of steam, dried, constricted near the open end, and weighed. By means of narrow thistle-funnels passed through the constriction in the test-tube, quantities of ethyl acetate and hydrochloric acid were introduced. The tube was weighed after each such addition, and then sealed off at the constriction, when it was immersed in a bath, kept at 25° ± 0·20°, and frequently shaken. The mixture became homogeneous after about one to two hours when 7·268N-hydrochloric acid was used, and the tubes were broken and their contents analysed after forty to fifty-eight hours; in experiments Nos. 1 and 4, however, thirty-five days elapsed before they were removed from the bath. When 0·1185N-hydrochloric acid was employed, complete admixture did not occur until after nearly three weeks, and in such cases the tubes were not removed before thirty-six days. The dried tubes were finally broken in excess of carefully neutralised sodium acetate solution, which was then diluted to a liter, portions of 100 c.c. being taken and titrated against standard baryta solution, with phenolphthalein as indicator. The amount of hydrogen chloride which remained was checked by means of standard silver nitrate. The results of the experiments are summarised in the table.

In line A are given the numbers of the experiments.
,, ,, B ,, ,, weights of ethyl acetate taken.
,, ,, C ,, ,, weights of 7·268N-hydrochloric acid.
,, ,, D ,, ,, weights of 0·1185N-hydrochloric acid.
,, ,, E ,, ,, amounts of hydrogen chloride taken in gram-molecules.
,, ,, F ,, ,, amounts of hydrogen chloride found at the end of the experiment.
,, ,, G ,, ,, total titre (acetic acid plus hydrogen chloride) in c.c. of normal acid.

In lines H, K, and L are given the total apparent number of gram-molecules of acetic acid (and alcohol), of water, and of ester, respectively, found at equilibrium.

In line R are given the ratios $[H_2O\ (total)]/[HCl]$ in each case.

In line S are given the values of ψ.

$$\psi = \frac{[H_2O\ (total)][CH_3 . CO_2 . C_2H_5]}{[CH_3 . CO_2H][C_2H_5 . OH]} .$$

The apparent value, $\psi = 4·35$, experiment No. 14, corresponds with the formation of 0·6761 gram-molecule of ethyl acetate and of water from 1 gram-molecule of acetic acid and of ethyl acetate. Berthelot and Péan de St. Gilles (*loc. cit.*) found that, at 9°, 1 gram-molecule of ethyl alcohol and of acetic acid combined to form 0·665 gram-molecule of ethyl acetate and of water, in the absence of hydrogen chloride ($[H_2O]/[HCl]$ = infinity).

No appreciable amount of ethyl chloride is formed under the conditions of the experiments.

The apparent value for the equilibrium constant varies from 4 to over 8 as the concentration of the hydrogen chloride increases.

A	1.	2.	3.	4.	5.	6.	7.	8.
B	12·3121	11·7921	11·3334	10·4887	11·1817	8·0458	7·0384	10·1819
C	2·0154	1·9992	3·9524	3·9337	4·6554	6·1489	4·2332	6·4593
D	—	—	—	—	—	—	—	—
E	0·01272	0·01265	0·02494	0·02482	0·02938	0·03880	0·02671	0·04076
F	0·0129	0·01264	0·0255	0·0255	0·0300	0·0397	0·0273	0·0419
G	40·04	39·30	63·68	62·05	71·27	78·81	58·20	87·32
H	0·02732	0·02665	0·03874	0·03723	0·04189	0·04001	0·03149	0·04656
K	0·05866	0·05884	0·1303	0·1306	0·1571	0·2230	0·1491	0·2295
L	0·1125	0·1073	0·0900	0·0820	0·0851	0·05142	0·04849	0·0690
R	4·61	4·65	5·22	5·26	5·35	5·75	5·58	5·63
ψ	8·83	8·90	7·81	7·73	7·62	7·17	7·29	7·30

A	9.	10.	11.	12.	13.	14.	15.
B	7·4224	5·811	5·3922	5·6624	3·9716	11·5222	11·0326
C	5·8523	7·6946	9·3930	11·0293	8·6004	—	—
D	—	—	—	—	—	4·4614	6·0886
E	0·03693	0·04855	0·05926	0·06958	0·05423	0·000528	0·000720
F	0·0371	0·0490	0·0610	0·0706	0·0542	—	—
G	74·42	84·35	96·02	109·8	83·43	57·38	63·04
H	0·03749	0·03580	0·03676	0·0402	0·02917	0·05685	0·06232
K	0·2127	0·2933	0·3648	0·4316	0·3386	0·1898	0·-744
L	0·04684	0·03032	0·02452	0·02414	0·01596	0·0741	0·06304
R	5·76	6·04	6·16	6·20	6·24	359·7	381·0
ψ	7·09	6·94	6·62	6·45	6·35	4·35	4·45

The apparent diminution in the active mass of the water corresponds with the formation of a compound having approximately the formula $HCl, 2H_2O$, or of compounds having that mean composition.

Another example of equilibrium is afforded by the action of ammonia upon ethyl acetate, acetamide and ethyl alcohol being produced according to the equation—

$$NH_3 + CH_3COOC_2H_5 \rightleftarrows CH_3CONH_2 + C_2H_5OH.$$

This has been investigated by Bonz (*Zeitsch. physik. Chem.*, **2**, 865, 1888), who showed, however, that the actual process is a more complicated one, for he succeeded in isolating ethyl ammonium acetate, ethyl acetamide, and water, in addition to the above.

A similar sort of difficulty was believed to exist in connection with the action of sulphuric acid upon ethyl alcohol, which on the simplest assumption should correspond to the equation—

$$C_2H_5OH + H_2SO_4 \rightleftarrows C_2H_5HSO_4 + H_2O.$$

The results obtained led Zaitschek (*Zeitsch. physik. Chem.*, **24**, 1, 1897) to conclude that the sulphuric acid existed in solution in the form of ortho sulphuric H_6SO_6. This conclusion is by no means convincing, and recent results of R. Kremann (*Monatshefte*, **31**, 245, 1910) go to show that the reaction is the simple one after all, the equilibrium constant—

$$K = \frac{C_{e\,\text{acid}} \times C_{e\,\text{alcohol}}}{C_{e\,\text{ester}} \times C_{eH_2O}}$$

having the value 1·74, and this happens to be practically independent of temperature (from 22° C. to 96° C.). The course of the reaction can scarcely yet, however, be regarded as definitely settled.

PHYSICAL PROPERTIES OF LIQUID MIXTURES.

When two completely miscible liquids, which do not visibly react with one another, are mixed together in any proportion, the physical properties of the mixture are found in general to differ from those calculated according to the simple mixture law. This divergence has been ascribed to changes in the state of aggregation of the molecules of one or both liquids, to the formation of a definite compound between the two liquids, or to both these causes combined

In spite of considerable investigation the problem of correlating in a quantitative manner the physical properties of a binary mixture with the chemical composition of the mixture is still largely unsolved. This is true not only of mixtures which contain at least one constituent which by itself is known to exhibit association (compare Chap. II.) but is even true of the much simpler case in which both constituents are normal, or nearly so.

The first attempt to deal in a quantitative manner with this problem was that of Dolezalek (*Zeitsch. physikal. Chem.*, 1908, also Dolezalek and Schulze, *ib.*, 1913). A further attempt is that of Dennison (*Trans. Faraday Soc.*, **8**, 1912), whose theoretical considerations have been recently tested in a number of cases by Hartung (*Trans. Faraday Soc.*, **12**, 66, 1917). The systems examined are: nitrobenzene + ether; aniline + ether; aniline + methyl alcohol; aniline + carbon tetrachloride. With the exception of methyl alcohol, these are normal or nearly normal liquids. The physical properties measured are: density and molecular volume, specific and molecular heats, and the heat effect on mixing. The conclusion arrived at by Hartung is that no single-solvate theory will suffice to explain the experimental results. In the great majority of cases the molecular condition of a mixture is very complex.

A systematic study of physical properties, including density viscosity, heat of reaction, heat capacity, and freezing point, in the case of a number of binary mixtures of phenols and organic bases has likewise been carried out by Bramley (*Trans. Chem. Soc.*, **109**, 424, 1916). Much more data of equal accuracy must be accumulated before any satisfactory theoretical advance is to be expected.

With regard to the general and often tacit assumption that deviations from the simple mixture law indicate chemical interaction, H. M. Dawson (*Annual Reports on the Progress of Chemistry*, **13**, 17, 1916) remarks: "It would seem very doubtful whether any of these properties can be made use of in a general way in the elucidation of the constitution of binary liquid mixtures". "This is not entirely or even mainly due to the disturbing influence of changes in the molecular complexity of the components, but to the incorrectness of the assumption that the simple mixture law is characteristic of mixtures in which there is neither chemical combination nor molecular dissociation. As a basis for the interpretation of property-composition curves, the straight line law is perhaps attractive on account of its simplicity, but this must not be confused with the plausibility of the hypothesis. The degree of plausibility will depend on the property considered, but in actual practice the hypothesis has been used in the interpretation of curves obtained by plotting all kinds of properties against the composition with practically no regard for the physical meaning of the curves These methods of dealing with experimental observations are bound to reveal inconsistencies, and in many cases to lead to fallacious conclusions." This is perhaps an extreme view to take, but it is well to point out the care which must be exercised in a problem of this kind.

2. SOLUTIONS.

It will be assumed that the reader is familiar with some of the ordinary physical properties of solutions, such as, the phenomena of saturation and super-saturation, diffusion of the dissolved substance or substances from places of high concentration to those of low, distillation and separation of constituents in certain cases by this means, as well as by freezing out part of the solvent, and so producing a more concentrated system. We may, therefore, pass on at once to consider the most important phenomenon exhibited by a solution, namely, the *osmotic pressure* of the solute or dissolved substance.

This is intimately connected with the diffusion or osmosis of the solute, since diffusion from high to low concentration is considered to take place in virtue of the existence of a force which when reckoned per unit area is called osmotic pressure. The earliest account of the phenomenon was given by the Abbé Nollet, who found that if a glass vessel be filled with spirits of wine, the opening tightly covered with a bladder, and the vessel immersed in water, then the volume of the contents of the vessel increases, so that the bladder is expanded and often burst. This experiment was repeated years later by Parrot in 1815, who came to the conclusion that all miscible liquids show a tendency to wander the one into the other, when they are brought into contact, and this process continues until the liquids are perfectly evenly distributed. For many years experiments were always made with animal membranes, until in 1867 Moritz Traube (*Archiv. f. Anat. und Physiol.*, p. 87) showed how chemical membranes could be made in the laboratory by precipitation. Traube showed that certain dissolved substances are able to pass through these membranes, whilst other substances cannot, but Traube did not measure the pressure effects produced by the phenomenon. Pfeffer, in 1877 (*Osmotische Untersuchungen*, Leipzig), was the first to carry out measurements of osmotic pressure. His apparatus consisted of a porous clay vessel, the walls of which served to support a precipitate of copper ferrocyanide—the precipitate is obtained embedded in the walls of the cylinder by placing a solution of potassium ferrocyanide inside and copper sulphate solution outside, and allowing both to diffuse into the walls, the precipitate being formed at the surface of contact. A cell of this kind allows water to pass freely through it, but prevents many dissolved substances, such as cane sugar in water. The arrangement is represented diagrammatically in the figure (Fig. 39). The cell is filled quite full with the solution of known strength, a manometer attached, and then the cell is immersed in pure water. It is found that water passes into the cell, thereby causing an increase in the pressure as indicated by the rise of mercury in the longer limb of the manometer. This goes on to a certain point until equilibrium is reached, at which the pressure[1] exerted downwards prevents any further water passing into the cell—more correctly, at this stage just as much water enters as leaves the cell per second. Very large pressures are often indicated, sometimes amounting to many atmospheres. The noteworthy fact in this connection is that the pressure registered, P, when equilibrium is attained depends on the concentration of the solute, being, according to Pfeffer, directly proportional to the concentration, provided the solution is not too strong. That is to say, that $\frac{P}{c}$ = constant, an expression which is quite analogous to Boyle's Law for gases. Pfeffer also observed that P varies directly as the absolute temperature, this behaviour being analogous to the Gay-Lussac-Charles Law. Further, it was observed that in many cases, *i.e.* when the solutes were non-electrolytes, the osmotic pressures produced by equimolecular concentrations of different substances were the same, indicating that Avogadro's principle was also applicable to dissolved substances. The laws of osmotic pressure are so important from the standpoint of the theory of solutions, that it is necessary to give some more detailed account of them, and in this connection the best method will be to quote a number of passages from a paper published by the late Prof. J. H. van 't Hoff, which appeared in Germany in 1887, summarising the results given in a number of papers presented to the Swedish Royal Academy of Sciences, in October, 1885. The English translation of this classical paper appeared in the *Philosophical Magazine*, 1888, where it is easily accessible to English readers. For the present we must restrict ourselves to the experimental side only. The thermodynamic treatment of the subject, which formed probably the most striking feature of van 't Hoff's work, must be postponed.

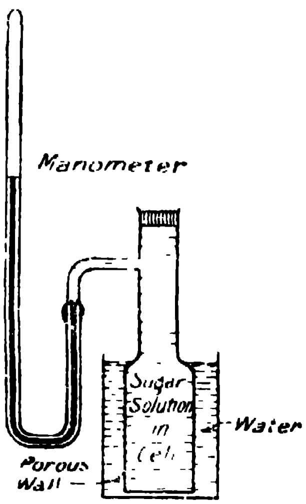


FIG. 39.

"During an investigation which required some knowledge of the laws regulating chemical equilibrium in solutions, the conclusion has gradually been evolved that a deep analogy—indeed, almost an identity

---

[1] Hydrostatic pressure due to the column of mercury and water.

—exists between dilute solutions exerting osmotic pressure on the one hand, and gases under ordinary atmospheric pressure on the other. The following pages contain an attempt to explain this analogy, and the physical properties of such systems will form the first subject of discussion.

" *Osmotic Pressure—the nature of the analogy due to this conception.*

"In order clearly to realise the quantity referred to as osmotic pressure, imagine a vessel A (Fig. 40) completely full of an aqueous solution of sugar, placed in water B. If it be conceived that the solid walls of this vessel are permeable to water, but impermeable to the dissolved sugar, then, owing to the attraction of the solution for water, water will enter the vessel A up to a certain limit, thereby increasing the pressure on the walls of the vessel [inside]. Equilibrium then ensues owing to the pressure resisting further entry of the water. This pressure we have termed *osmotic pressure.* It is evident that this state of equilibrium might have been attained in A without entry of water if the vessel had been constructed with a piston compressing the solution with a pressure equal to the osmotic pressure (Fig. 41). It follows, moreover, that by increasing or diminishing the pressure on the piston the state of concentration of the liquid [solution] can also be altered owing to the passage of water through the walls of the vessel in an outward or inward direction. Such osmotic pressure has been experimentally investigated by Pfeffer [*l.c.*]." We are already familiar with his experimental arrangement. "As an example of the results obtained it may be mentioned that a 1 per cent. solution of sugar (which, owing to its considerable mass, was not appreciably diluted on entry of water) exerted at 6·8° C. a pressure of 50·5 mm. mercury—about $\frac{1}{15}$th atmosphere. The porous membrane such as that described will be termed in the following pages a 'semi-permeable' membrane; and the conception will be made use of even when experimental verification is lacking. The behaviour of solutions may thus be studied in a manner strictly analogous to that employed in the study of gases, inasmuch as what is known as 'osmotic pressure' corresponds to the pressure, or as it is commonly but incorrectly termed, the 'tension' of a gas. It is right to mention that this is no fanciful analogy, but a fundamental one." Van 't Hoff restricts his conclusions to *ideal solutions*, that is to say, solutions so dilute that the action of the dissolved molecules upon one another, as well as their actual volume compared with that of the space they inhabit, is so small

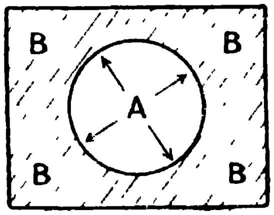


FIG. 40.

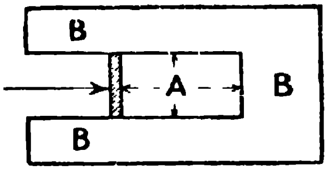


FIG. 41.

as to be negligible; that is to say, an ideal solution is analogous to an ideal gas. In practice, of course, we can only work—even in the most dilute cases—with approximation to this ideal state.

"*Boyle's Law for Dilute Solutions.*—The analogy between dilute solutions and gases acquires at once a quantitative form, if it be noted that in both cases alteration of concentration exercises a similar influence on pressure, and is in both cases proportional to the pressure. This proportionality, which for gases goes by the name of Boyle's Law, may be proved experimentally for liquids [*i.e.* solutions] as well as deduced theoretically.

"[*Direct*] *Experimental proof.* (Determination of osmotic pressure for solutions of various concentrations.)

"Let us first adduce Pfeffer's determinations (*l.c.*, p. 71) of the osmotic pressure P in sugar solutions at [approximately] the same temperature (13·2° to 16·1° C.) and with varying concentration *c*.

c.	P.	$\frac{P}{c}$.
1 per cent.	535 mm.	535
2 ,,	1016 ,,	508
2·74 ,,	1518 ,,	554
4 ,,	2082 ,,	521
6 ,,	3075 ,,	513

The approximately constant quotients $\frac{P}{c}$ point conclusively to this proportionality between pressure and concentration.

"*Comparison of Osmotic Pressures by Physiological Methods.*—Observations of de Vries (*Eine Methode zu Analyse der Turgorkraft*, Pringsheims Jahrbuch 14) show that equal changes of concentration of solutions of sugar and of potassium sulphate and nitrate exercise equal influence on the osmotic pressure. This osmotic pressure was compared, by physiological methods, with that of the contents of a plant cell; the protoplasmal envelope contracts when it is immersed in solutions possessing great attraction for water. By a systematic comparison of the three bodies mentioned, using the same cells, three *isotonic liquids* (*i.e.* liquids [solutions] exhibiting the same osmotic pressure) were obtained. Cells of a *different* plant were then made use of, and so four isotonic series were constructed [by the help of four different plant cells] which showed a similar proportion in their concentrations; this is exhibited in the following table, where the concentrations are expressed, first in gram-molecules per liter, and then referred to potassium nitrate as unity."

Series.	KNO_3.	$C_{12}H_{22}O_{11}$.	K_2SO_4.	$KNO_3 = 1$.	$C_{12}H_{22}O_{11}$.	K_2SO_4.
I.	0·12	—	0·09	1	—	0·75
II.	0·13	0·2	0·1	1	1·54	0·77
III.	0·195	0·3	0·15	1	1·54	0·77
IV.	0·26	0·4	—	1	1·54	—

If van 't Hoff's idea held quite generally for all dissolved substances, one would have expected that the second half of the table would simply consist of a series of the same number, namely, one.

Reasons for the discrepancy—which is *not* due to inherent error in van 't Hoff's conception—will be given when we come to study electrolytic dissociation. The above results show, however, that the effects are independent of the nature of the membrane, since different plant cells were employed, and this is in agreement with van 't Hoff's view.

Theoretical Proof.—"These observations render highly probable the existence of proportionality between osmotic pressure and concentration, and the theorem may be completed by a theoretical proof which is indeed almost self-evident." "Regarding osmotic pressure as due to a kinetic cause (*i.e.* as produced by impacts of the dissolved molecules [upon the inside of the semi-permeable membrane]), there must exist a proportionality between the number of impacts in unit time and the number of molecules in unit volume. The proof is therefore exactly the same as that for Boyle's Law." "If, on the other hand, osmotic pressure be regarded as the outcome of an attraction for water molecules, its value is evidently proportional to the number of attracting molecules in unit volume, provided (and this is taken for granted in sufficiently dilute solutions) the dissolved molecules exercise no attraction on each other, and each one exerts its own special attractive action uninfluenced by its neighbours." Such a view would equally lead to the conclusion that a law analogous to that of Boyle should hold for dilute solutions. Granted that such a force is acting outwards (provided the solution be placed *inside* the porous pot and semi-permeable membrane), it is clear that the solution tends to increase in volume, and this it can do if the opportunity be given for water to stream in from the outside through the membrane. By this process the solution tends to dilute itself, *i.e.* the *water* concentration tends to become identical on both sides of the membrane. If there were no membrane present, or if the membrane were equally permeable to solute and solvent, the solute would diffuse out until finally the whole system would be equally concentrated with respect to solute, and therefore equally concentrated with respect to solvent. It seems reasonable to suppose, therefore, that when diffusion of a solute does occur in a given direction, it is due to the osmotic pressure acting as the driving force. Of course we cannot speak of the osmotic pressure of the solvent, but simply of the solute, since the concentration of the solute corresponds to gas concentration.

"*Gay-Lussac's Law for Dilute Solutions.*—While the proportionality between concentration and osmotic pressure is self-evident so long as the temperature remains constant, the proportionality between osmotic pressure and absolute temperature, the concentration being maintained constant, is not so manifest. Yet proof can be furnished from thermodynamic considerations; and experimental data exist which are highly favourable to the results predicted on thermodynamic grounds.

"*Experimental Proof.* (Determination of the osmotic pressure at different temperatures.)—Pfeffer (*l.c.* pp. 114-115) found that the osmotic pressure increases with rise in temperature. It will be seen that although his results do not furnish a conclusive proof of the correctness of the theorem, yet there is a most striking correspondence between experiment and theory. If we calculate from one of two experiments at different temperatures the osmotic pressure to be expected in the other by the help of Gay-Lussac's Law and compare it with the experimental result, we have the following series:—

I. Solution of cane sugar.		
Pressure at 32° C. found . . .	544	mm.
Pressure at 14·15° C. calculated	512	„
„ „ „ found . .	510	„
II. Solution of cane sugar.		
Pressure at 36° C. found . . .	567	„
Pressure at 15·5° C. calculated . .	529	„
„ „ „ found . .	520·5	„
III. Solution of sodium tartrate.		
Pressure at 36·6° C. found . .	1564	„
Pressure at 13·3° C. calculated . .	1443	„
„ „ „ found . .	1431·6	„
IV. Solution of sodium tartrate.		
Pressure at 37·3° C. found . .	983	„
Pressure at 13·3° C. calculated . .	907	„
„ „ „ found . .	908	„

"*Comparison of the Osmotic Pressure by Physiological Methods.*—In the same manner that support has been lent to the application of Boyle's Law to solutions (*viz.* that different substances in *isotonic* solutions retain their equality of osmotic pressure, so long as their respective concentrations are reduced to the same fraction), so the application of Gay-Lussac's Law receives support by the fact that this isotonic state is maintained during equal alterations of temperature. It has been proved by physiological methods by Donders and Hamburger (*Onderzoekingen gedaan in het physiol. Laborator. der Utrechtsche Hoogeschool* [3], **9**, 26), making use of blood corpuscles, that solutions of potassium nitrate, sodium chloride, and sugar, which at 0° C. are isotonic with the contents of these cells, exhibit the same isotonic state at 34° C.; this is seen in the annexed table:—

	Temperature 0° C.	Temperature 34° C.
KNO_3 .	1·052 to 1·03 per cent.	1·052 to 1·03 per cent.
NaCl .	0·62 „ 0·609 „	0·62 „ 0·609 „
$C_{12}H_{22}O_{11}$.	5·48 „ 5·38 „	5·48 „ 5·38 „

"*Experimental Proof of Boyle's and Gay-Lussac's Laws for Solutions.*—Experiments by Soret (*Archives des sciences phys. et nat.* [3], ii., p. 48; *Annales de Chim. et de Phys.* [5], **22**, 293).

"The phenomenon observed by Soret lends a strong support to the analogy between dilute solutions and gases in respect of the influence of concentration and temperature on pressure. His work shows that just as in gases the warmest part is the most rarefied, so with solutions the warmest portions are the most dilute; but that in the latter case a much longer time must be allowed for the attainment of equilibrium. The experimental apparatus consisted of a vertical tube, the upper portion of which was heated while the lower portion was kept at a low temperature.

"Soret's latest experiments lend a quantitative support to our analogy. As with gases, it is to be expected, that when the isotonic state is produced the solution will exist in equilibrium; and as the osmotic pressure is proportional to concentration and absolute temperature, the isotonic state of different portions of the solution will occur when the products of the two (absolute temperature and concentration) are equal. If we therefore calculate on this basis the concentration of the warmer part of the solution from data obtained from the colder, the values compare with those found as follows:—

"1. Solution of copper sulphate. The portion cooled to 20° C. contained 17·332 per cent. The hot portion at 80° C. should contain 14·3 per cent.; found 14·03 per cent.

"2. The portion cooled to 20° C. contained 29·867 per cent. The portion at 80° C. should contain 24·8 per cent.; found 23·871 per cent.

"It must be stated that previous experiments by Soret gave less favourable results; yet perhaps too much importance should not be attached to them, owing to the difficulties of experiment." In addition to the experimental evidence cited by van 't Hoff mention may be made of an optical method of determining isotony of solutions by Tammann (*Wied. Ann.*, **34**, 299, 1888). The method is based on the use of the Töpler apparatus for detecting small changes in the refractive powers of liquids or solutions. A Pfeffer cell is set up containing a solution of some substance inside and immersed in a solution of another substance. If the concentrations are such that the solutions are isotonic, no solvent will pass from one side to the other. If the solutions are not isotonic, solvent will pass either inward or outward, causing thereby a change in concentration or "streaming" near the wall which can be detected by the change in the refractive index. It is thus possible to adjust one liquid to the other in respect of concentration of solute so that no change in refractive index is observed. Tammann used copper ferrocyanide and zinc ferrocyanide membranes. He compared copper salts and zinc salts against potassium ferrocyanide. In the following table are given data which show that the *ratio* of the isotonic concentrations does not change much with increasing dilution. On van 't Hoff's assumption it should not change at all as long as the solutions in all cases may be described as dilute.

Isotonic Solutions. Concentration in Gram-molecules per 1000 Grams H_2O.		Ratio $\frac{\text{Concentration of } CuSO_4}{\text{Concentration of } K_4Fe(CN)_6}$.
$CuSO_4$.	$K_4Fe(CN)_6$.	
0·842	0·313	2·7
0·675	0·240	2·8
0·339	0·117	2·9
0·204	0·079	2·6
0·170	0·066	2·6
0·094	0·036	2·6

The method can be further extended by adding to one of the solutions, say the $CuSO_4$, some third substance and then finding what concentration of ferrocyanide is isotonic with the mixed solution. That part of the osmotic pressure which is due to the substance added can then be calculated on the supposition (the accuracy of which it would be possible to establish by the experiments themselves) that the osmotic pressure of the mixed substances is the sum of the pressures of each, *i.e.* Dalton's Law.

Avogadro's Hypothesis applied to Dilute Solutions.—Avogadro's hypothesis states that one mole of a gas at a given temperature and pressure occupies the same volume as one mole of any other gas at the same temperature and pressure, provided, of course, that abnormal effects such as dissociation are absent. Having found that Boyle's and Gay-Lussac's Laws hold for dilute solutions, van 't Hoff was led to the assumption that Avogadro's hypothesis would likewise hold for dilute solutions, *i.e.* under equal osmotic pressures and at the same temperature equal volumes of different solutions would contain equal numbers of solute molecules, or equimolecular solutions at the same temperature should exert the same osmotic pressure; and further, if a solution exerts an osmotic pressure, say, of P atmospheres at a given temperature, there are just as many *solute* molecules in a given volume of the solution as there would be gas molecules in the same volume of gas, supposing the gas also exerted P atmospheres pressure at the above temperature.

The well-known formula expressing both Boyle's and Gay-Lussac's Laws for gases—

$$pv = RT$$

is, in so far as these laws are applicable to liquids [solutions], also applicable as regards osmotic pressure; with the reservation, also made in the case of gases, that the space occupied by the molecules must be so great that the actual volume of the molecules becomes negligible. If Avogadro's hypothesis be also introduced, it may be expressed in the above equation by giving to R a certain numerical value, namely, 1·98 (or 2·0 approximately), the unit of energy being the calorie, the unit of mass of gas considered being one mole. It is to van 't Hoff that we owe the idea that this gas equation is directly applicable to solutions, the value of R being identical with its value for gaseous bodies.

"*First Confirmation of Avogadro's Hypothesis in its application to Solutions—Direct Determination of Osmotic Pressure.*—It is to be expected that Avogadro's hypothesis deduced as a consequence of Henry's Law for solutions of gases, will not be restricted to solutions of substances which usually exist in a gaseous condition. This expectation has been realised, not merely from a theoretical, but from an experimental standpoint. Pfeffer's determinations of the osmotic pressure of solutions of sugar furnish a remarkable proof of this extension of the hypothesis.

"Pfeffer's solution consisted of 1 gram of sugar dissolved in 100 grams of water; 1 gram of the sugar therefore exists in about 100·6 c.c. of the solution."

The number of moles of sugar in 100·6 c.c. is therefore $\frac{1}{342}$ (since $C_{12}H_{22}O_{11} = 342$). The concentration is therefore $\frac{1 \times 1000}{342 \times 100{\cdot}6}$, or 0·02906 mole per liter. Let us now calculate what pressure would be exerted by hydrogen gas, say (molecular weight 2) at 0° C. and at the above concentration. One liter of hydrogen gas weighs 0·08956 gram at 0° C. when its pressure is one atmosphere. That is, its concentration in moles per liter is $\frac{0{\cdot}08956}{2}$, or 0·04478. Since gas pressure is proportional to concentration, it is evident that at a concentration of 0·02906 mole per liter the hydrogen would only exert a pressure of $\frac{0{\cdot}02906}{0{\cdot}04478}$, or 0·649 atmosphere at 0° C. Similarly, at any temperature t the pressure will be $0{\cdot}649\,(1 + 0{\cdot}00367t)$. Placing these results beside Pfeffer's, we obtain the following agreement:—

Temperature t.	Osmotic Pressure.	Gas Pressure under same Conditions. $0{\cdot}649\,(1 + 0{\cdot}00367t)$.
6·8	0·664	0·665
13·7	0·691	0·681
14·2	0·671	0·682
15·5	0·684	0·686
22·0	0·721	0·701
32·0	0·716	0·725
36·0	0·746	0·735

The directly determined osmotic pressure of a solution of sugar is thus seen to be equal to the pressure of a gas at the same temperature, containing the same number of molecules in unit volume as the sugar solution.

"Starting from cane sugar, this relation can be calculated for other dissolved substances, such as invert sugar, malic acid, tartaric acid, citric acid, magnesium malate and citrate, all of which from de Vries' physiological researches (*Eine Methode zur Messung der Turgorkraft*) exhibit equal osmotic pressure, when they contain an equal number of molecules in a given volume."

Besides the evidence for the applicability of the gas laws cited by van 't Hoff, one may mention Tammann's results (*l.c.*), in which it was found that in aqueous solutions of cane sugar, salicin, ethyl alcohol, urea, propyl alcohol, equimolecular solutions possessed the same osmotic pressure within the limits of experimental error. Tammann further pointed out that solutions with the same osmotic pressure possess the same vapour pressure—a statement which we shall come to presently in van 't Hoff's paper.

The most accurate verification of the applicability of the gas laws to dilute solutions at various temperatures is furnished by the work of Morse and Frazer and their collaborators (*Journ. Amer. Chem. Soc.*, 1907-1912). In the work of 1908 the osmotic pressures of aqueous solutions of sucrose were determined at 10° C. and 15° C., solutions of dextrose at 20° C. Considerable difficulty was met with in the preparation of satisfactory semi-permeable membranes, and the success of the work really lay in overcoming this. The results are accurate to the first place of decimals. Previous measurements had led to the belief that the osmotic pressure at 0° C. was substantially the same as at 20° C., but it was shown in the paper referred to that there is undoubtedly a temperature coefficient of osmotic pressure, and that this coefficient is practically identical with the temperature coefficient of gases. This work is especially remarkable for the elaborate care with which it was carried out, and consequently the trustworthiness of the results, some of which are here tabulated (see next page).

If van 't Hoff's assumptions held rigidly, the ratios just given should be unity. Though not unity, they are at least constant.

In 1909 the experiments at 20° and 25° C. were published. The values of the ratio, mean osmotic pressure to gas pressure, were 1·069 at 20° C. and 1·064 at 25° C.

The results obtained more recently[1] (1912) show that the 0·1 N solution between 30° C. and 60° C., and the 0·2 N solution between 50° C. and 60° C. obeys Gay-Lussac's Gas Law *strictly*.

It has already been mentioned that the ratio of mean osmotic to gas pressure, which should be unity if Boyle's Law held at the same time, is a little larger than unity. This tends, however, towards and eventually

---

[1] H. N. Morse, W. K. Holland, C. N. Myers, G. Cash, J. B. Zinn, *Amer. Chem. Journ.*, 48, 29, 1912.

OSMOTIC PRESSURE OF SUCROSE SOLUTIONS.

Concentration (Weight Normal, *i.e.* Gram-molecules of Solute per 1000 grams of Solvent).	Temperature.			
	0° C.	4° to 5° C.	10°.	15°.
	atmos.	atmos.	atmos.	atmos.
0·1	2·42	2·40	2·44	2·48
0·2	4·79	4·75	4·82	4·91
0·3	7·11	7·07	7·19	7·33
0·4	9·35	9·43	9·58	9·78
0·5	11·75	11·82	12·00	12·29
0·6	14·12	14·43	14·54	14·86
0·7	16·68	16·79	17·09	17·39
0·8	19·15	19·31	19·75	20·09
0·9	21·89	22·15	22·28	22·94
1·0	24·45	24·53	25·06	25·42
Mean "molecular osmotic pressure," *i.e.* pressure due to one mole solute per 1000 grams solvent.	23·95	24·12	24·50	24·98
Mean "molecular gas pressure," *i.e.* pressure due to one mole of gas in a volume equal to that occupied by 1000 grams of water at the temperature in question.	22·29	22·65	23·09	23·50
Ratio: mean osmotic pressure to gas pressure.	1·074	1·065	1·061	1·064

becomes unity at higher temperatures, *i.e.* the solutions at higher temperatures become more "ideal". Boyle's Law, for example, holds *exactly* in the following cases:—

Up to 0·2 N solutions at 50° C.
„ 0·4 N „ 60° C.
„ 0·7 N „ 70° C.
„ 1·0 N „ 80° C.

The work carried out by Morse and his collaborators may be regarded as completely satisfactory proof that dilute solutions do obey the gas laws. Investigation upon more concentrated solutions has shown, on the other hand, that the simple gas laws do not hold at all accurately just as they do not hold for highly compressed gases.

We have been considering the direct evidence for van 't Hoff's assumption regarding the applicability of the gas laws (including the Avogadro hypothesis) to solutions. The next point taken up by van 't Hoff is the "*Second confirmation of Avogadro's hypothesis in its application to solutions. Molecular lowering of vapour pressure.*" We must digress a little at this point in order to consider some of the experimental results obtained in connection with the lowering of the vapour pressure.

It was known for many years that water which contains some non-volatile substance dissolved in it boils at a higher temperature than pure water. The boiling point is simply the temperature at which the vapour pressure of the liquid is equal to atmospheric pressure; and since the vapour pressure always increases with rise of temperature, the existence of a raised boiling point (in the case of a solution) indicates that the presence of the solute has lowered the vapour pressure of the solvent. The first generalisation made in this connection is that of von Babo (1848), who found that the relative lowering of vapour pressure, namely, $\frac{p_0 - p_1}{p_0}$ [where p_0 is the vapour pressure of the pure solvent at a given temperature, and p_1 the vapour pressure of a solution (having the same solvent, of course) at the same temperature], is independent of the temperature provided the solution is dilute.

Wüllner (*Poggendorff's Ann.*, **103**, 529, 1858; **105**, 85; **110**, 56, 1860) came to the conclusion that the lowering of the vapour pressure of water by non-volatile solutes is proportional to the concentration of the solute. The later work of Tammann showed that the law of proportionality was not strictly accurate. It is important to note that the substances examined by these investigators were salts, *i.e.* electrolytes, in aqueous solution. A great deal of apparent contradiction and lack of uniformity was removed, however, when Raoult[1] commenced his classic work on the behaviour of non-electrolytes, organic substances, dissolved in organic solvents. Raoult employed the barometric method for determining the vapour pressure.

Employing ether as solvent, Raoult was able to confirm von Babo's Law, namely, that the fractional lowering of vapour pressure $\frac{p_0 - p_1}{p_0}$ is independent of the temperature. He also found that for solutions of medium concentration the fractional lowering of vapour pressure is proportional to the concentration—which is Wüllner's Law. The most important advance, however, made by Raoult lay in the introduction of the "molecular lowering" of vapour pressure, *i.e.* he compared the lowering produced by equimolecular quantities of different solutes in the same solvent. If M is the molecular weight of the solute, x the mass of solute in grams dissolved in 100 grams of ether, then *the "molecular lowering" c_1 was found to be a constant for the solvent employed*, namely, ether. c_1 is given by the expression—

$$c_1 = \frac{p_0 - p_1}{p_0} \cdot \frac{M}{x}.$$

---

[1] *Comptes Rendus*, 103, 1125, 1886. The work was actually begun in the 'seventies and continued for a number of years without publication.

The following table contains some of Raoult's data (solvent ether):—

Solute.	M.	c_1.
Carbon hexachloride	237	0·71
Turpentine	136	0·71
Methyl salicylate	152	0·71
Cyanic acid	43	0·70
Benzoic acid	122	0·71
Trichlor acetic acid	163·5	0·71
Benzaldehyde	106	0·72
Caprylic alcohol	130	0·73
Cyanamide	42	0·74
Aniline	43	0·71
Antimony trichloride	228·5	0·67

Some of these solutes scarcely correspond to the condition of non-volatility even at ordinary temperatures—the solvent ether happened to have a considerable vapour pressure in comparison, however. The molecular lowering of vapour pressure, *i.e.* the lowering produced by one mole of any solute in a given amount of solvent, is independent of the nature of the solute. The lowering of the vapour pressure depends therefore on the number of solute molecules present, not on the kind of molecule. When, however, aqueous solutions of salts are examined, one no longer obtains a constant as in the above, unless, indeed, we compare salts of closely analogous type, *e.g.* $CuSO_4$, $ZnSO_4$, etc., in which case an approximate constant is obtained having a different numerical value from that given above. This circumstance no doubt prevented earlier observers from arriving at Raoult's generalisation. Raoult also discovered the following relationship in 1887 (*C. R.*, **104**, 1430), that the lowering of vapour pressures of different *solvents* is the same when the ratio of the number of molecules of solute to molecules of solvent is the same.

In connection with the "molecular lowering" mentioned above it will be well to give at least one instance of the results obtained by Raoult (*Zeitsch. physik. Chem.*, **2**, 353, 1888) as evidence of the same law put in a slightly different form. Thus if n is the number of solute molecules dissolved in N molecules of solvent, then the concentration of the solute molecules expressed as a fraction of the total molecules present may be written $\frac{n}{N+n}$, which for dilute solutions (N large compared to n) may be expressed as $\frac{n}{N}$. Raoult found the following relation to hold—

$$\frac{p_0 - p_1}{p_0} = \frac{n}{N + n}.$$

This expression gives the relation between the fractional lowering of vapour pressure and the concentration of the solution, the concentration being expressed in molar fractions. The degree of agreement between the two sets of values is shown in the following table in which the solute is aniline and the solvent ether:—

$100\frac{n}{N+n}$.	$100\frac{p_0-p_1}{p_0}$.	$100\frac{n}{N+n}$.	$100\frac{p_0-p_1}{p_0}$.
3·85	4·0	20·5	19·7
7·7	8·1	49·6	42·4
14·8	15·4	68·7	59·6

The relationship discovered by Raoult may be used to determine the molecular weight of the solute, assuming the molecular weight of the solvent is known. That is, if a certain mass of solution is known to contain N moles of solvent, we can calculate n if we measure the lowering of vapour pressure due to the presence of the solute. If m grams of solute are actually present and M is its molecular weight in solution, evidently $n = \frac{m}{M}$, whence M can be calculated. As a matter of fact, the method of measurement of lowering of vapour pressure has been very little used for the determination of molecular weights until recently Menzies has improved the technique (see Vol. II., Chap. VI.). The usual methods for molecular weight determination are those which are closely allied to the lowering of vapour pressure on theoretical grounds, namely, the "lowering of freezing point" and the "rise of boiling point" methods.

Returning to van 't Hoff's argument, it will be remembered that he considers the numerical data obtained in the case of the "molecular lowering of vapour pressure" as the second confirmation of the application of Avogadro's law to solutions. He does this by showing by means of thermodynamics the relationship which must exist between the osmotic pressure of the solution (*i.e.* of the solute in the solution) and the lowering of vapour pressure of the solvent owing to the presence of the solute. Instead of following the thermodynamical reasoning (which will be taken up in Vol. II., Chap. VI.) we shall consider the problem from the kinetic standpoint by a method first proposed by Arrhenius in 1889 (*Zeitsch. physik. Chem.*, **3**, 115, 1889). Suppose we have a tube[1] having a semi-permeable membrane fixed at

---

[1] The tube is not a capillary one, nor is the surface of the solution curved as in the case of the somewhat similar arrangement due to Lord Kelvin for the determination of the change of vapour pressure of a pure liquid with curvature.

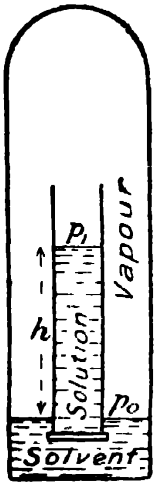


FIG. 42.

the lower end and partly filled with a solution of cane sugar in water, the tube dipping into pure water as shown in the figure (Fig. 42). Water enters the tube until the solution forms a column of height h. Suppose equilibrium is attained at that point, *i.e.* suppose that the hydrostatic pressure of the column of solution which tends to drive solvent downwards through the membrane just balances the osmotic pressure P of the solution which has caused the entry of water upwards. Let ρ be the mean density of the solution, this being practically the density of the solvent if the solution is dilute. Let σ be the mean density of the vapour over the range h. In the actual case the density of the vapour alters with the height. We are dealing with a simplified case which is only approximately true. Let p_0 be the value of the vapour pressure over the solvent and p_1 that over the solution. The hydrostatic pressure of the liquid column acting downwards is $h\rho g$. At the equilibrium this is balanced by P. That is—

$$P = h\rho g.$$

But considering an imaginary column of vapour also of height h, the hydrostatic pressure of the vapour is $h\sigma g$, and this must be identical with the difference of the vapour pressures at the top and bottom of the column, namely, $p_0 - p_1$.

Hence $$p_0 - p_1 = h\sigma g.$$

Therefore $$p_0 - p_1 = P\frac{\sigma}{\rho}.$$

Now σ may be written $\frac{m}{v}$, where m is the molecular weight and v is the molecular volume of the vapour, *i.e.* the volume of one mole. Suppose as a first approximation that the vapour obeys the gas law, *i.e.* $p_0 v = RT$ or $\sigma = \frac{m}{v} = p_0\frac{m}{RT}$.

Then after substitution one obtains—

$$\frac{p_0 - p_1}{p_0} = \frac{Pm}{\rho RT}.$$

Since at a given (constant) temperature ρRT is constant (as long as the different solutions do not vary too much in concentration, *i.e.* as long as their densities are approximately that of the solvent), one may write—

$$\frac{p_0 - p_1}{p_0} \propto P$$

i.e. the fractional lowering of vapour pressure is proportional to the osmotic pressure. Now van 't Hoff's theory may be expressed in the equation—

$$P = RTc$$

where c is the concentration of the solute or the reciprocal of the dilution. If there are n moles of solute dissolved in V litres of solution, $c = \frac{n}{V}$. It follows that—

$$\frac{p_0 - p_1}{p_0} = \frac{Pm}{\rho RT} = \frac{mn}{\rho V} = \frac{n}{\frac{\rho V}{m}} = \frac{n}{N},$$

since $\frac{\rho V}{m} = N$, the number of moles of solvent in which n moles of solute are dissolved. The above result is Raoult's relation. The fact that the application of Avogadro's hypothesis to dilute solutions permits of the deduction of Raoult's experimental relation, is evidence for the applicability of the hypothesis.

As already mentioned, closely connected with the phenomenon of the lowering of vapour pressure is that of the "elevation of boiling point". The elevation is directly proportional to the lowering of the vapour pressure, and since it has been found fairly easy to make accurate determinations of changes in boiling point by Beckmann's method, this may be used to calculate the molecular weight of the dissolved substance. In this phenomenon, the application of Avogadro's hypothesis leads to the statement that equi-molecular concentrations of various solutes in the same solvent cause the same elevation of boiling point. This has been verified experimentally, and may be likewise deduced on thermodynamic grounds. The discussion of the deduction and its use in the determination of molecular weight must be postponed.

We now pass on to van 't Hoff's "*third confirmation of Avogadro's Law in its application to solutions. The molecular depression of freezing point of the solvent,*" due to the presence of the solute. We shall look for a moment at some of the earlier researches. The earliest investigation of the subject was carried out by Blagden in 1788 (*Phil. Trans. Roy. Soc.*, **78**, 277), who showed that the depression of freezing point of aqueous solutions of a given substance below the freezing point of water was proportional to the concentration of the substance in solution. Blagden's work did not attract any attention. His generalisation was rediscovered independently by Rüdorff in 1861, but it was only in 1871 that attention was drawn by Coppet to the earlier work. In the case of the solutions thus investigated, and those which we are about to mention in more detail, it is important to remember that when freezing takes place it is the pure solid solvent which crystallises out. This is likewise the case considered by van 't Hoff. If the solute separates out simultaneously with solvent to form a *homogeneous* mass called a "solid solution," or "mixed crystal," or, on the other hand, if solvent and solute separate out to give a heterogeneous conglomerate (crystals of both lying side by side), such being known as a cryohydric mixture, we can no longer—on theoretical grounds—expect the simple relationship to hold. For the verification of the van 't Hoff assumption we must deal only with those solutions from which pure solvent separates out on freezing. It happens that this includes by far the larger number of cases so far investigated. It should be mentioned that the work of Coppet and Rüdorff referred to, while supporting Blagden's general conclusion, also brought to light many examples of apparently abnormal behaviour, *e.g.* in the case of strong acids, bases, and salts in aqueous solution, which served to show that the phenomenon was rather a complicated one, and it was not until the theory of electrolytic dissociation was put forward by Arrhenius (1883) that an explanation of many of these abnormalities was forthcoming. The work of Raoult, begun several years previously and published in 1882 (*Compt. Rend.*, **94**, 1517, 1882; *ibid.*, **95**, 188, 1030, 1882), in which organic substances were employed as solutes in aqueous solution, served to bring out the important relationship *that the molecular depressions of freezing point were nearly the same for the various solutes when dissolved in one and the same solvent*, *e.g.* water. Raoult extended his investigations to other solvents, and again obtained a series of new constant molecular depressions. (Raoult had also noticed certain abnormalities in the case of water when this was the solvent.) The results of his work were published in detail in the *Annales de Chim. et de Physique* [5], **28**, 137, 1883; *ibid.* [6], **2**, 66, 1884. Defining the molecular depression of freezing point as the lowering produced by one gram molecular weight (one mole) of the solute in 100 grams of solvent, we find that the following data (taken from the very extended tables given by Raoult), bear out his statement:—

SOLUTIONS IN BENZENE.		SOLUTIONS IN WATER.	
Solute.	Molecular Depression.	Solute.	Molecular Depression.
Methyl iodide	50·4	Urea	17·2
Nitrobenzene	48·0	Acetamide	17·8
Naphthalene	50·0	Ethyl acetate	17·8
Anthracene	51·2	Tartaric acid	19·5
		Acetic acid	19·0
		Cane sugar	18·5
Ethyl alcohol	28·2	Ethyl alcohol	17·3
Methyl alcohol	25·3		
Phenol	32·4		
Acetic acid	25·3	Hydrochloric acid	39·1
Benzoic acid	25·4	Nitric acid	35·8
		Caustic potash	35·3
		Potassium chloride	33·6
		Sodium chloride	35·1

A glance at the table shows that for one and the same solvent we may divide solutes in respect of molecular depressions of freezing point into at least two sets—indicated by the dotted lines. An abnormally *small* depression could be brought about by *association* of some of the solute molecules together, for the depression is proportional to the *number* of solute particles present in a given volume, and so, although we may have added a mole of solute in grams, owing to a number of these being associated say to produce molecules of double the normal molecular weight, there are fewer individuals present than we would normally anticipate, and hence the depression produced is abnormally small. This is true, for example, in the case of solutes containing hydroxyl groups, alcohols, acids, etc., or cyanogen groups when dissolved in benzene.[1] On the other hand, abnormally great depression was attributed later by Arrhenius (*Zeitsch. physik. Chem.*, 1887) to electrolytic dissociation, which had suggested itself to him some four years previously, and according to which a molecule of an electrolyte can give rise to two or more electrically charged atoms or ions, *i.e.* individuals are present in greater number than would be normally expected from the mass of substance dissolved, thereby causing the abnormally great depression. This is characteristically the case with inorganic acids, bases, and salts in aqueous solution, such solutions possessing at the same time the property of conducting the electric current, the solute being therefore called an "electrolyte". Substances which do not conduct current are known as "non-electrolytes". Arrhenius' explanation was, however, necessarily unknown to van 't Hoff when he first brought out his osmotic theory of solution; so that quantitative support to his theory could only be obtained from *some* of Raoult's values, namely, those which are now regarded as "normal," in which the solute molecules are neither associated nor dissociated. It is the great merit of Arrhenius' theory of electrolytic dissociation that it offers an explanation of the abnormally great depressions observed with inorganic acids, bases, and salts in aqueous solution, which is in quantitative accord with the osmotic theory of solution.

The striking feature in favour of van 't Hoff's argument as regards the phenomenon of molecular depression, is that he actually calculated by thermodynamic means what the normal constant should be for substances dissolved in a given solvent. The formula obtained by van 't Hoff applies equally well to the molecular rise of boiling point, provided corresponding meanings are attached to the symbols. The expression referred to may be written—

$$\delta = \frac{0{\cdot}02T^2}{L}$$

where δ stands for the molecular lowering of freezing point, or molecular rise of boiling point.

T is the absolute temperature of freezing or boiling of the solvent.

L is the latent heat of fusion, or latent heat of vaporisation per gram of the solvent.

Van 't Hoff goes on to say: "This theoretical deduction receives ample confirmation from experimental data. The following table exhibits the molecular depression of freezing point experimentally determined by Raoult, along with the values calculated by means of the above formula :—

---

[1] This can be shown, for example, by applying Nernst's theory of the distribution of a solute between two immiscible solvents (*cf.* Chap. VII.),

Solvent.	Freezing Point, T° abs.	Latent Heat of Fusion, L.	δ Calculated, *i.e.* $\delta = \frac{0{\cdot}02T^2}{L}$.	Molecular Depression Observed by Raoult.
Water . .	273	79 cals.	18·9	18·5
Acetic acid .	273 + 16·7	43·2 ,,	38·8	38·6
Formic acid .	273 + 8·5	55·6 ,,	28·4	27·7
Benzene . .	273 + 4·9	29·1 ,,	53	50
Nitrobenzene .	273 + 5·3	22·3 ,,	69·5	70·7

This part of the subject has been extended at a later date by Eykmann (*Zeitsch. physik. Chem.*, **3** and **4**, 1889).

NOTE.—It may be well at this juncture to point out that a connection between lowering of freezing point, rise of boiling point, and depression of vapour pressure had been established prior to van 't Hoff's work, though not upon so general a basis. In 1878 Raoult (*Compt. Rend.*, **87**, 167, 1878) showed empirically with regard to 18 salts, which he had examined with respect to their effect on the freezing point and boiling point of the solvent, that the effects were proportional to one another. The relation thus empirically established by Raoult had been deduced theoretically some years before by Guldberg (*Compt. Rend.*, **70**, 1349, 1870) by a thermodynamic method. The merit of showing the interconnection of these phenomena with osmotic pressure rests with van 't Hoff. It should be clearly understood that although we have followed van 't Hoff's paper in which his theory is put forward, we have necessarily restricted ourselves to experimental evidence only. As a matter of fact, however, the great value which attaches to van 't Hoff's work rests on its thermodynamical basis, for although thermodynamics had been introduced into chemistry some years previously by Horstmann (1869), van 't Hoff's conception of osmotic pressure and the application of the laws of thermodynamics to "osmotic work," have laid the foundation of the greater part of physical chemistry as it exists to-day.

Before leaving this part of the subject it is of interest to discuss briefly *the application of Avogadro's hypothesis to aqueous solutions of inorganic acids, bases and salts.*

The generalisation which van 't Hoff found to hold true for dilute solutions of numerous substances—principally organic substances—in various solvents may be written—

$$P = RTc$$

where P is the osmotic pressure produced by the solute the concentration of which is c (stated as a rule in moles per liter, or sometimes per 1000 grams of solvent). For inorganic acids, bases, and salts[1] in aqueous solution this simple osmotic law does not hold if we ascribe to R the value it has in the case of gases. P is greater, twice or thrice as great in some cases, as the expression RTc. This has manifested itself in the allied phenomena of lowering of freezing point and rise of boiling point.

---

[1] The salts may also contain an organic acid radicle, *e.g.* sodium acetate.

To get over the difficulty van 't Hoff suggested the inclusion of an empirical factor *i*, which he regarded in the first instance as a constant. The osmotic law of van 't Hoff for solutions of these substances takes the form $P = iRTc$. The factor *i* was shown later by Arrhenius, on the basis of the electrolytic dissociation theory, not to be constant but to increase as the concentration of the solute diminishes. The following table contains a few of the data given by Arrhenius in 1888 (*Zeitsch. physik. Chem.*, **2**, 496, 1888). They refer to determinations of lowering of the freezing point—denoted by Δt—for since the lowering is proportional to P it is likewise proportional to $iRTc$. When a "normal" solute such as cane sugar is used, *i.e.* one for which $i = 1$, and the simple expression $P = RTc$ holds good, it is easy to calculate what the normal values of Δt ought to be, and the ratio of the observed Δt to the calculated value gives *i* directly.[1]

SOLUTIONS OF SODIUM CHLORIDE IN WATER.

c in Moles per Liter.	Δt Observed.	*i*.
0·0467	− 0·117°	2·00
0·117	− 0·424	1·93
0·194	− 0·687	1·87
0·324	− 1·135	1·86
0·539	− 1·894	1·85

SOLUTIONS OF SODIUM SULPHATE IN WATER.

c in Moles per Liter.	Δt Observed.	*i*.
0·0280	0·141	2·66
0·0701	0·326	2·46
0·117	0·515	2·33
0·195	0·817	2·21

The important point to note is that these substances, which on being dissolved give rise to solutions with abnormally great osmotic pressure, are electrolytes. This makes us at once suspect that there is some close connection between the two sets of phenomena. This will be taken up in the succeeding chapter. Before going on with the phenomena of electrolytic dissociation, however, it is convenient to discuss briefly one or two instances of reactions between the molecules of the solvent and the molecules of the solute present together in the solution.

In dealing with solutions it has already been said that many of the reactions which occur in them may be treated without special reference to the solvent itself. In some cases, however, the solvent actually plays a definite *rôle*, though it must be remembered that even where the solvent is not considered it is by no means to be inferred that it is perfectly inert. In general, as a matter of fact, there must be some kind of interaction between solvent and solute, even in cases where it is not easy or even possible to demonstrate it. The type of reaction to be considered at this point is, however, one in which it has been possible to show that the solvent is taking a definite chemical part, although so far the methods employed to investigate this sort of phenomenon have not been particularly fruitful except in certain cases. An instance of these reactions is the formation of molecular hydrates (assuming the solvent to be water), that is, compounds formed between a molecule of the solute and one or more molecules of the solvent. Similarly there is evidence to show that ions (present, say, when an inorganic acid, base, or salt is dissolved in water) may in certain cases be hydrated. There is likewise the widespread phenomenon of hydrolysis of salts dissolved in water. Reactions involving ions will be considered in the following chapter. For the present we shall only consider by way of illustration,[1] a mixture of ethyl alcohol and water from the standpoint of possible union between the molecules to give compounds. Reference may, first of all, be made to the work of Mendeléef, who determined the density of numerous mixtures of alcohol and water of different percentage composition, and concluded from the irregular nature of the curve as we pass from 100 per cent. water to 100 per cent. alcohol that several complexes, *i.e.* molecular compounds, exist in solution. The work of Jones (*Zeitsch. physik. Chem.*, **13**, 419, 1894), however, who carried out a series of freezing point determinations at various concentrations, afforded no evidence for any complex formation. The variation of other physical properties with composition of the solution or mixture has been employed to try and settle the question. Thus the ***viscosity*** of alcohol-water mixtures reaches a ***maximum*** at a point corresponding to the composition $C_2H_5OH,3H_2O$. Such evidence alone must not be taken, however, as actually proving the existence of the complex ($C_2H_5OH,3H_2O$), for we have no ***a priori*** reason for believing that the formation of a complex will necessarily increase the viscosity, and still more when we take into account the further experimental fact that the *position* of the maximum, *i.e.* the composition of the mixture which possesses maximum viscosity, *varies gradually with the temperature.* Now the criterion of a true compound is that its composition should not show any gradual change with change of conditions, such as temperature and pressure. The results of viscosity measurements afford little conclusive evidence, though they are sufficient to show that the system is behaving in a rather remarkable fashion. More definite are the recent results obtained by Dorochewski and Roshdestwenski (*Journ. Russ. Phys. Chem. Soc.*, **40**, 860, 1908), using the electrical conductivity method. They showed that the electrical conductivity passes through a ***minimum*** (as we alter the concentration progressively) at about 50 per cent. alcohol, and, according to Kohlrausch—who has given reasons for believing that a compound does not conduct so well as a solution—this should really indicate formation of a compound having the composition ($C_2H_5OH,3H_2O$). Of course, an obvious difficulty crops up, in that we are accustomed to regard water and alcohol as non-conductors. This is approximately correct, but they give rise to a few ions. The resistances met with in these Russian investigators' experiments were very large indeed. Mention must also be made of the work of Hess (*Annalen der Physik*, **27**, 609, 1908), who found that the volume contraction resulting from the addition of alcohol to water showed a maximum at about 50 per cent. water, *i.e.* at a composition corresponding approximately to ($C_2H_5OH,3H_2O$). It is probable, therefore, that this hydrate exists to a very large extent, but the most correct view to take of the whole question is to look upon these complexes as labile compounds, or rather to consider that there are a very large number of different hydrates present, some of which are more stable than others, and exist in larger quantity and therefore affect certain physical properties. These hydrates are in equilibrium with one another at a certain temperature, but with change in this condition there is a corresponding shift in the equilibrium points, so that those which predominate at one temperature may no longer do so at another. It is hopeless, however, to try and apply the principle of mass action to a system so complicated as this.

---

[1] This mode of procedure is open to serious criticism (*cf.* Vol. II., Chap. VIII.).

---

[1] This subject is treated in a very interesting manner by Arrhenius in his book, *Theories of Chemistry.*

Another typical instance of complex formation is met with in mixtures of sulphuric acid and water. A study of the physical behaviour of this system, in spite of much conflicting evidence, has yielded the result that the hydrates (H_2SO_4,H_2O) and ($H_2SO_4,2H_2O$) fairly certainly exist in comparatively large quantity, the first being the more stable. This conclusion has been reached as a result of Jones' (*Zeitsch. physik. Chem.*, **13**, 419, 1894) investigations upon the freezing points of mixtures of sulphuric acid and water.

Before leaving the subject of molecular complexes attention should again be drawn to the care which must be exercised in taking some abnormality in a physical property as evidence for the existence of a compound. Thus take the phenomenon of boiling. It is well known that constancy of boiling point is one of the best tests of the purity of a substance, *i.e.* evidence that we are dealing with a single substance and not a mixture. Chemists were so familiar with this test that they concluded that the constant boiling mixture of water and hydrochloric acid, which corresponds in composition to the formula $HCl + 8H_2O$, was actually a true compound. It was shown, however, by Roscoe (*Journ. Chem. Soc.*, **12**, 128; *ib.*, **13**, 146, 1860) that this view is not correct. Roscoe distilled aqueous solutions of HCl at different pressures, namely, at 5, 70, 80, and 150 cms. mercury. The *composition* of the mixture possessing a maximum boiling point—and therefore boiling at constant temperature when once this stage was reached—was found to differ according to the pressure at which the distillation was carried out. Thus at 76 cms. mercury the mixture possessing the maximum boiling point contained 20·24 per cent. hydrochloric acid, while the corresponding mixtures at the pressures mentioned contained 23·2, 20·4, 20·2, and 18·2 per cent. HCl respectively. Now since a chemical individual must possess the same composition under different conditions (Dalton's Law), Roscoe concluded that the constant boiling solutions of $H_2O + HCl$ were not compounds but mixtures, and that therefore the constancy of boiling point affords no proof at all in the above case that a compound $HCl + 8H_2O$ exists.

The simplest type of hydrate formation which could exist is that represented by the equation—

$$A + n(H_2O) \rightleftarrows A(H_2O)_n$$

if A be the only solute present. Suppose that the above reaction occurs and that equilibrium is reached—as is usual in such cases—practically instantaneously. Let c be the concentration of the hydrated molecules $A(H_2O)_n$ in moles per liter, c_1 the concentration of non-hydrated molecules of the solute A, and c_2 the concentration of the water molecules.

Applying the law of mass action, the relation follows—

$$\frac{c_1 \times c_2^n}{c} = \text{a constant} = K.$$

Now as long as the solution is dilute, the concentration of the water may be regarded as constant, and this term may therefore be brought over into the constant K, which now takes on a new value, K_1, in which—

$$K_1 = \frac{c_1}{c}.$$

That is to say, the concentration of the hydrated molecules bears a constant ratio to the unhydrated molecules; in other words, the fraction of solute molecules hydrated, or the "degree of hydration," is independent of the actual concentration of the solution, *i.e.* the degree of hydration is the same in a decinormal solution as it is in a centinormal one, though, of course, in the first case, the actual concentration of hydrated and unhydrated molecules is much the greater. Nernst, in his text-book, has pointed out that this conclusion respecting degree of hydration is often overlooked. It is, however, a logical consequence of the application of the law of mass action to dilute systems of this kind.

THE LAW OF MASS ACTION IN DILUTE SOLUTIONS.

The law of mass action, as expressed in the equilibrium constant, is shown in Vol. II., Chap. V., to depend upon the osmotic pressure of each of the constituents participating in the reaction. Further, it is shown that the law can only be expected to be accurately true for chemical equilibria in systems in which the osmotic pressure of each constituent obeys the gas law PV = RT. We have already seen that the gas law only applies to dilute solutions. It follows, therefore, that we are only justified in applying the law of mass action to dilute solutions. From this standpoint the reactions considered in the early part of this chapter can only be expected to show an approximate agreement with the law of mass action. To investigate the law under legitimate conditions it is necessary to deal with a reaction which has attained equilibrium in a dilute solution, the solvent being regarded as inert in the sense that it does not enter explicitly into the stoicheiometric equation of the reaction.

CHAPTER V.

Chemical equilibrium in homogeneous systems (*continued*)—Mechanism of electrolytic conduction in solutions—The theory of electrolytic dissociation applied to aqueous solutions—Electrolytic dissociation in non-aqueous solutions.

ELECTROLYSIS. FARADAY'S LAW.

THE first fact in connection with electrolytic solutions or solutions containing one or more electrolytes is that such solutions obey Ohm's Law just as metallic conductors do. The second fact is that in solutions the transfer of electricity differs from that in metallic conductors in that the passage of the current is accompanied by a transference of matter towards the electrodes. The matter so transferred may or may not be "discharged" or set free at the electrode. Thus the electrolysis of an aqueous solution of copper sulphate, using copper electrodes, causes metallic copper to be precipitated upon the cathode (the negative electrode), an equivalent quantity of copper dissolving off the anode (the positive electrode), the positive electrode being that at which current enters the electrolysis bath, the negative electrode that at which it leaves. Using platinum electrodes in the same solution metallic copper is again precipitated upon the cathode, while at the anode oxygen gas is liberated. The oxygen is formed by the discharge of a number of OH' ions, which are already present as a result of the ionisation of water, thus, $H_2O \rightarrow H^{\cdot} + OH'$. Faraday introduced the idea of "*ions*," that is to say, electrically charged atoms or radicles. The solution as a whole is electrically neutral, and therefore there must be exactly as many positive ions as negative ions. The process of electrolytic dissociation of molecules into ions may be represented in the case of potassium chloride by the equation—

$$KCl \rightarrow \underset{\text{Potassium ion.}}{K^{+}} + \underset{\text{Chlorine ion.}}{Cl^{-}}$$

or, in the more usual form, $KCl \rightarrow K^{\cdot} + Cl'$. These ions, Faraday considered, conduct the current, the positive ion ($K^{\cdot}$) travelling towards the cathode, the negative ion (Cl') travelling towards the anode. Faraday discovered two quantitative laws of electrolysis which now bear his name. They are:—[1]

(*a*) The voltametric law, which asserts that the amount of electrochemical decomposition is a precise measure of the amount of electricity conveyed.

---

[1] Compare Lodge, *Brit. Ass. Report*, 1885, p. 756.

(*b*) The law of electrochemical equivalence, which asserts that when a current is sent through a series of different substances, the mass of each substance liberated (or decomposed, or dissolved, or whatever happens to it) is proportional to its ordinary chemical equivalent.

These laws may be summed up in the expression—

$$w = zct$$

where w = weight of a constituent (say, copper in the $CuSO_4$ case) precipitated on the cathode.

z = the electrochemical equivalent of the copper, *i.e.* the quantity precipitated by unit current flowing per unit time. The electrochemical equivalent of any element is = the electrochemical equivalent of hydrogen × chemical equivalent of the element in question.

c = current.

t = time.

It is not necessary to go into the fundamental phenomena in any further detail, since this is assumed to be familiar to the reader; we may therefore pass on to the theory which professes to account for the conducting property possessed by solutions of electrolytes, namely, the theory of electrolytic dissociation, especially in regard to its bearing on osmotic phenomena and the van 't Hoff empiric factor.[1]

To understand Arrhenius' argument more clearly, it is necessary to refer to the work of Kohlrausch on the subject of conductivity, and especially his law of 1876 regarding the equivalent conductivity of acids, bases, or salts at infinite dilution being made up of two separate parts, one referring to the anion, the other to the cation.

The usual method adopted for measuring the resistance (or its reciprocal, the conductivity) of an electrolytic solution consists in employing an alternating current from a small coil and using a telephone in place of a galvanometer. The object of the alternating current is to do away with polarisation effects on the electrodes, *i.e.* changes in resistance and E.M.F. due to chemical effects which accompany the processes occurring at the electrodes when a direct current is used. The principle adopted in the measurements is simply that of the Wheatstone Bridge, which is represented diagrammatically in Fig. 43.

R is the known resistance; X the resistance of the solution; AB is a metre wire, and the connection with the telephone D is made by a sliding contact to the wire C, which is moved about until no sound is any longer heard in the telephone, balance between R and X having then been obtained. Frequently the arrangement is slightly different, *i.e.* telephone D and coil E are interchanged. The advantage is a practical one, in that full current is always passing through the bad

---

[1] Any who wish to study from the historic standpoint the subject of electrolysis and the theories put forward, should consult the Report of the Electrolysis Committee of the British Association at their 1885 meeting.

(sliding) contact C. The proper balance is obtained when no current flows through the telephone, *i.e.* A *viâ* E to B, in the alternative arrangement to that shown in the figure. In both cases the relationship holds:—

$$\frac{R}{AC} = \frac{X}{BC} \text{ or } X = R \cdot \frac{BC}{AC}.$$

The specific conductivity l of an electrolyte = the current which flows when the electrolyte is between electrodes 1 square cm. area, 1 cm. apart, with a P.D. of 1 volt between the electrodes.

"For[1] one and the same electrolyte this specific conductivity is naturally very much dependent on the concentration, since, as it varies, the amount of the electrolyte, contained in the 1 centimetre cube between the electrodes, must vary. The study of the specific conductivity can therefore give directly no means for finding out in what way the molecule of the substance changes its capacity for conducting electricity with varying dilution. Such a means is gained, however, from the specific conductivity, if we reduce the same by calculation to one and the same concentration—for instance, to one equivalent in the centimetre cube." That is to say, if we divide the observed specific conductivity of the unit cube of liquid by the concentration of the solute in gram equivalents per c.c. we get a quantity to which the name equivalent conductivity is applied. It is the same thing to say that the equivalent conductivity is equal to the specific conductivity observed multiplied by the volume which contains one gram equivalent of the solute at the particular dilution in question. In this way we are always dealing with the conductivity due to the same *mass* of solute, and any variation in the numbers obtained must be due to some change in the *nature* of the solute individuals in the solution. Ostwald imagines the same state of affairs to be reached by picturing electrodes which remain at a fixed distance apart, 1 cm., but which with increasing dilution of

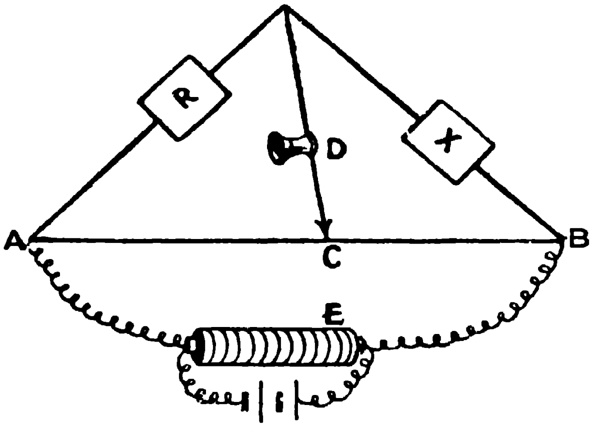


FIG. 43.

---

[1] Quotation from Abegg's *Electrolytic Dissociation Theory*.

the electrolyte always increase in area, so that the volume of liquid included between the electrodes always contains just one equivalent of the electrolyte. The conductivity of one equivalent (*i.e.* the "equivalent conductivity") at various dilutions is evidently a magnitude capable of giving information as regards change in the molecular condition in so far as this influences the conductivity. Since the specific conductivity is the observed conductivity of the unit cube, it is evident that as we increase the dilution we cause fewer individuals to exist between the electrodes in the cell, and though these individuals may alter somewhat in their molecular condition, *i.e.* may give rise to ions to a greater extent, their number has decreased so much that the observed conductivity also decreases. The specific conductivity therefore decreases as we increase the dilution. On the other hand, the equivalent conductivity (*i.e.* the specific conductivity reduced always to what it would be if one gram equivalent of the electrolyte was pushed between the electrodes, and supposing further that the molecular condition remained just as it was before the imaginary compressing process took place)—the equivalent conductivity was found by Kohlrausch to increase with increasing dilution, and in many cases reached a limit at very great dilution—such cases being solutions of the good electrolytes, *viz.* inorganic acids, bases, and salts in general. The limiting value here indicated is known as the equivalent conductivity at infinite dilution, and is represented by the symbol Λ_∞. Now conductivity had been long ascribed to positive and negative ions. Further, the work of Hittorf has shown that these ions move under the same potential gradient with different velocities in aqueous solutions, $H^{\cdot}$ and OH' being by far the fastest. *Kohlrausch's relation of* 1876 *is known as the law of the independent migration of the ions.* He found that Λ_∞ could be written as the sum of two effects, one due to the anions, the other to cations. He called these the mobilities of the cation and anion respectively, and denoted them by U and V, *i.e.* $\Lambda_\infty = U + V$. He based this relationship on the purely additive character of the equivalent conductivities which he observed.[1]

His law means that the mobility of $Na^{\cdot}$, for example, should have the same value whether derived from chlorides or nitrates, etc. He verified it by showing that the following held true:—

$$\{\Lambda_\infty NaCl - \Lambda_\infty KCl\} = \{\Lambda_\infty NaNO_3 - \Lambda_\infty KNO_3\}.$$

We see that the law is in agreement with this experimental fact, because—

$$\begin{aligned}\Lambda_\infty NaCl &= U_{Na^{\cdot}} + V_{Cl'}\\ \Lambda_\infty KCl &= U_{K^{\cdot}} + V_{Cl'}\\ \Lambda_\infty NaNO_3 &= U_{Na^{\cdot}} + V_{NO'_3}\\ \Lambda_\infty KNO_3 &= U_{K^{\cdot}} + V_{NO'_3}\end{aligned}$$

---

[1] For a discussion of the mechanical friction of the solvent see a paper by Kohlrausch, *Proc. Roy. Soc.*, 71, 338, 1903.

and therefore

$$\Lambda_\infty \mathrm{NaCl} - \Lambda_\infty \mathrm{KCl} = U_{\mathrm{Na}^\cdot} + V_{\mathrm{Cl}'} - U_{\mathrm{K}^\cdot} - V_{\mathrm{Cl}'} = U_{\mathrm{Na}^\cdot} - U_{\mathrm{K}^\cdot}$$

$$\Lambda_\infty \mathrm{NaNO_3} - \Lambda_\infty \mathrm{KNO_3} = U_{\mathrm{Na}^\cdot} + V_{\mathrm{NO'_3}} - U_{\mathrm{K}^\cdot} - V_{\mathrm{NO'_3}} = U_{\mathrm{Na}^\cdot} - U_{\mathrm{K}^\cdot}$$

The following numerical data are taken from the extended list given by Kohlrausch (Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*). The value of Λ_∞ was found to have reached its limit when the concentration of solute was $\frac{\mathrm{N}}{1000}$.

Salt.	Λ_∞.	Therefore, assuming Kohlrausch's Law to be true—
KCl . . .	129·1	$U_{\mathrm{K}^\cdot} - U_{\mathrm{Na}^\cdot} = 21·0$
NaCl . .	108·1	
$\mathrm{KNO_3}$ . .	125·5	,, = 20·9
$\mathrm{NaNO_3}$ . .	104·6	
$\mathrm{KIO_3}$ . .	97·6	,, = 20·9
$\mathrm{NaIO_3}$ . .	76·7	
$\frac{1}{2}\mathrm{K_2SO_4}$.	133·5	,, = 23·0
$\frac{1}{2}\mathrm{Na_2SO_4}$.	110·5	

The constancy of $(U_{\mathrm{K}^\cdot} - U_{\mathrm{Na}^\cdot})$ is borne out by these results. To show, by way of illustration, how equivalent conductivity varies with concentration, finally reaching a limit, one may take Kohlrausch's values for KCl at 18° C. (data of 1885):—

Concentration of Salt in Gram Equivalents per Liter	Λ.	Difference Between Successive Values of Λ
1	98·2	13·7
0·1	111·9	10·6
0·01	122·5	5·1
0·001	127·6	1·9
0·0001	129·5	
$\frac{1}{\infty}$	131·2 (extrapolated)	

Now let us turn to the work of Arrhenius. His fundamental idea is that electrolytic dissociation is a function of concentration. That is to say, it is partial at ordinary concentration, and increases as we increase the dilution (*i.e.* as we decrease the concentration), becoming practically complete at infinite dilution. It will be seen how this at once gives a new significance to the rather empiric mobilities of Kohlrausch. The limiting value of the molecular or equivalent conductivity is simply reached, according to Arrhenius, when the dissociation into ions is practically complete. Not only did Arrhenius state these generalisations, but he also quantitatively made use of conductivity measurements to determine the degree of electrolytic dissociation of the solute at any given dilution. He assumed that the conductivity due to the solvent was practically nil, and ascribed all the effects to the ions of the solute. This is in agreement with experiment, in so far at least as observation goes on the conductivity of pure water, which is extremely small.

CALCULATION OF DEGREE OF DISSOCIATION BY COMBINING ARRHENIUS' THEORY WITH KOHLRAUSCH'S LAW.

By the degree of dissociation (α) is meant the fraction of each gram-molecule of solute which is decomposed into ions. Suppose that at a certain dilution we say the degree of dissociation is 0·5. This simply means that one-half of the solute is still in the undissociated molecular state, the other half having given rise to two or more ions according to its nature, *i.e.* according to the number of atoms composing the molecule, although it must not be understood from this that the ions produced are always as numerous as the atoms from which they might be produced. Thus Na_2SO_4 gives three ions, $Na^{\cdot}$, $Na^{\cdot}$, SO_4''. (Note the double charge in the ion which corresponds to the valency of the group. The solution as whole, however, is electrically neutral.) On the other hand, H_2SO_4, at certain concentrations, gives mainly $H^{\cdot}$ and HSO_4', while at greater dilution we get increasing quantities of SO_4''. To show how α may be calculated we proceed as follows: In a given solution into which two electrodes dip—the electrodes being 1 square c.m. area and 1 cm. apart—a certain e.m.f. E is maintained between them by some external means. The current which flows is given by Ohm's Law, *i.e.* $C = \frac{E}{R}$, or El_v, where l_v is specific conductivity at this dilution, and is the reciprocal of the specific resistance. We may also view the process of current from the actual ionic effects taking place. Suppose the solution contains 1 gram-equivalent of a salt such as KCl dissolved in v c.c., then $\frac{1}{v}$ is the concentration, and supposing the gram-equivalent of the salt to be fractionally dissociated to the extent α into two sorts of ions, *viz.* Cl′ and $K^{\cdot}$, we have therefore $(1 - \alpha)$ undissociated gram-equivalents, and α equivalents of anions and α equivalents of cations. Let u_c be the absolute velocity of the cation under a potential gradient of one volt/cm., then under E volt/cm. the velocity is Eu_c. Similarly let v_a be the velocity of the anion. Let F be the charge associated with each univalent gram ion, then F will be likewise the charge carried by one equivalent of any ion. The current transported per second across an imaginary plane of unit area parallel to the electrodes is made up of the sum of the parts due to cation and anion respectively. The quantity carried per second by the cation is :—

$$\frac{1}{v}\alpha FEu_c$$

in one direction, while in the opposite direction the anion transports—

$$\frac{1}{v}\alpha FEv_a$$

and therefore the total current is—

$$\frac{1}{v}\alpha\mathrm{FE}(u_c + v_a)$$

and this must be equal to $\mathrm{E}l_v$.

Suppose now we work at a very great dilution, so that there is complete dissociation, $\alpha = 1$. Then under the same conditions of applied e.m.f. E to the same cell the current is—

$$\frac{1}{v_\infty}\mathrm{FE}(u_c + v_a) \text{ or } \mathrm{E}l_\infty.$$

Hence

$$\frac{\mathrm{E}l_v}{\mathrm{E}l_\infty} = \frac{\frac{1}{v}\alpha\mathrm{FE}(u_c + v_a)}{\frac{1}{v_\infty}\mathrm{FE}(u_c + v_a)}$$

or

$$\alpha = \frac{l_v \times v}{l_\infty \times v_\infty}$$

but $l_v \times v$ = the equivalent conductivity at dilution $v = \Lambda_v$

$l_\infty \times v_\infty$ = " " infinite dilution $= \Lambda_\infty$

$$\therefore \alpha = \frac{\Lambda_v}{\Lambda_\infty}.$$

This is Arrhenius' equation, and by its means he carried out a long series of calculations upon Kohlrausch's data for many sorts of electrolytes at various concentrations.

We are now in a position to appreciate how Arrhenius was able to explain the behaviour of those substances which had been found by van 't Hoff to be at variance with the simple osmotic law $\mathrm{P} = \mathrm{R}Tc$, and for which he had introduced the empirical form $\mathrm{P} = i\mathrm{R}Tc$. It will be more satisfactory to use Arrhenius' own words. For that purpose, portion of a paper of his which appeared in 1887 is here inserted, in which the subject of the osmotic pressure of electrolytes is discussed on the basis of the theory which he had put forward in 1883.

TRANSLATION OF PORTION OF A PAPER BY ARRHENIUS "ON THE DISSOCIATION OF SUBSTANCES DISSOLVED IN WATER".[1]

"In a paper presented to the Swedish Academy of Sciences on October 14, 1885, van 't Hoff demonstrated, both theoretically and by experimental results, the following extremely important generalisation and extension of Avogadro's Law:—

"'The pressure which is exerted by a gas at a given temperature, when a certain number of molecules are distributed throughout a given volume, is numerically identical with the osmotic pressure which would be exerted under the same circumstances by the majority of substances when these are dissolved in any liquid.'

---

[1] *Zeitsch. für physik. Chem.*, 1, 631, 1887.

"This law van 't Hoff has demonstrated in a manner which scarcely allows any doubt to exist as regards its general correctness. However, a certain difficulty, which still remains to be removed, is that while the law holds good 'for the majority of substances,' at the same time a remarkably large number of the aqueous solutions which have been examined form exceptions in the sense that they exhibit a much greater osmotic pressure than is predicted by the above law.

"Now, when a gas exhibits anomalous behaviour of this kind with regard to Avogadro's Law, an explanation is usually found in the assumption that the gas is in a state of dissociation.

"A well-known example of this is afforded by the behaviour of Cl_2, Br_2, and I_2 at high temperatures, under which circumstances these bodies are considered to be split up into simple atoms.

"The same explanation naturally suggests itself in regard to the exceptions to van 't Hoff's Law. This has, however, not yet been accepted, probably on account of its novelty, and on account of the many known difficulties and objections which would be raised against such an explanation on chemical grounds. The object of the following paper is to show that the assumption of dissociation in the case of certain substances dissolved in water, is supported to a very great degree by the conclusions which can be drawn from the electrical behaviour of these substances, and further, on closer inspection, the objections on purely chemical grounds are seen to be much diminished.

"One must assume with Clausius (*Pogg. Ann.*, **101**, 347, 1857; *Wiedemann's Elektricität*, **2**, 941), in order to explain electrolytic phenomena, that a fraction of the molecules of an electrolyte is dissociated into ions, which possess the property of independent movement and migration. Since now the osmotic pressure, which a dissolved substance exerts against the walls of the containing vessel, must be considered in agreement with the modern kinetic theory, *as arising from the impacts which the smallest individual parts of this body cause by their movements against the sides of the vessel*, so one must further assume, in order to be in agreement with this, that a molecule completely dissociated in the above manner, exerts against the side of the vessel a pressure identical with what would be exerted by its ions in the free state. If one therefore could calculate, how great a fraction of the molecules of an electrolyte is dissociated into ions, one could also calculate the osmotic pressure by means of van 't Hoff's Law.

"In an earlier paper 'On the Conduction of Electricity by Electrolytes,' I have applied the term 'active' to those molecules whose ions are free to move independently of one another, and the term 'inactive' to those molecules whose ions are firmly bound together. Further, I have suggested the probability that in extremely great dilution all the inactive molecules of an electrolyte are converted into active (*Bihang der Stockholmer Akad.*, **8**, No. 13, 14. Two parts, June, 1883). I shall make this assumption the groundwork of the following calculations.

The ratio of the number of active molecules to the sum of *active*[1] and *inactive* molecules is denoted by the term activity coefficient. The activity coefficient of an electrolyte at infinite dilution is therefore taken to be unity. For less dilution (*i.e.* greater concentrations), it is less than unity, and according to the principles on which my work referred to is based, in the case of not too concentrated solutions (that is to say, solutions in which disturbing conditions such as changes in internal friction, etc., can be neglected) the coefficient can be put equal to the ratio of the actually observed value of the molecular [or equivalent] conductivity to its limiting value, towards which it tends on continually increasing the dilution.

"If this activity coefficient (α) is known, one can *calculate* the values of the coefficient (i) tabulated by van 't Hoff. The coefficient (i) [or in English, as it is more frequently called, 'van 't Hoff's Factor'] is the ratio of the osmotic pressure actually exerted by a body to the osmotic pressure it would have exerted had it simply consisted of inactive (non-dissociated) molecules.

"Evidently i is equal to the sum of inactive molecules plus the number of ions, the sum being divided by the number {active molecules[2] plus inactive molecules}. Thus if there are m inactive molecules and n active molecules present, and k represents the number of ions into which *one* active molecule can dissociate, then—

$$i = \frac{m + kn}{m + n}.$$

"For KCl, $k = 2$, namely $K^{\cdot}$ and Cl'; for $BaCl_2$, $k = 3$, namely $Ba^{\cdot\cdot}$, Cl', Cl'; and so on.

"Since the activity coefficient α is evidently equal to $\frac{n}{m + n}$,

we have $$i = 1 + (k - 1)\alpha$$

in short, $$i = \frac{\text{number of } \textit{individuals} \text{ actually present}}{\text{number of individuals which would be present if no dissociation had taken place.}}$$

"The figures in the last column of the following table have been calculated by the aid of the above formula.

"On the other hand, one can calculate i according to van 't Hoff (as follows from the results obtained by Raoult on the freezing points of solutions), namely, by taking the lowering of freezing point of water[3]—say t° C.—brought about by dissolving 1 gram-molecule of a given substance in 100 grams of water and dividing t° by 18·5°. The values for $i = \frac{t}{18\cdot5}$ are given in the following table. The values given below are calculated on the assumption—as was actually fulfilled in the experiments of Raoult—that 1 gram-molecule of the substance under examination is dissolved in 10 litres of water." [1] The following table contains only a few of the data collected by Arrhenius. It is to be understood that the values of "a" are all obtained by the electrical conductivity method, *i.e.* $a = \frac{\Lambda_v}{\Lambda_\infty}$.

---

[1] Note that active molecules have no real existence as molecules; they represent the part which has been changed into ions.

[2] Note the distinction between active molecules and ions. Thus in the case of KCl *two* ions ($K^{\cdot}$ and Cl') can be produced from one active molecule. As already stated, the existence of active molecules is imaginary.

[3] This mode of treating freezing-point data is criticised later (Vol. II., Chap. VIII.).

BASES DISSOLVED IN WATER.

Substance.	a.	$i = \frac{t}{18\cdot5}$.	$i = 1 + (k - 1)a$.
Barium hydroxide	0·84	2·69	2·68
Strontium hydroxide	0·86	2·61	2·72
Sodium hydroxide	0·88	1·91	1·88
Potassium hydroxide	0·93	1·79	1·93
Ammonium hydroxide	0·01	1·00	1·01
Methylamine (methyl ammonium hydroxide)	0·03	1·09	1·03
Aniline (anilinium hydroxide) . . .	0·00	[1]	[1]

ACIDS DISSOLVED IN WATER.

Substance.	a.	$i = \frac{t}{18\cdot5}$.	$i = 1 + (k - 1)a$.
Hydrochloric	0·90	1·98	1·90
Hydriodic	0·96	2·03	1·96
Nitric	0·92	1·94	1·92
Sulphuric	0·60	2·06	2·20
Sulphurous	0·14	1·03	1·28
Hydrogen sulphide	0·00	1·04	1·00
Boric	0·00	1·11	1·00
Acetic	0·01	1·03	1·01
Oxalic	0·25	1·25	1·50
Tartaric	0·06	1·05	1·12

---

[1] There appears at first sight to be some confusion regarding the concentration of the dissolved substances. One mole of solute in 100 grams of solvent is in many cases quite unrealisable in practice owing to solubility limitations. The solution examined is much more dilute, the lowering of freezing point actually observed being altered by simple proportion to the value it would have supposing 1 mole of solute were dissolved in 100 grams of solvent, the solute remaining in the same molecular condition as in the dilute case.

SALTS DISSOLVED IN WATER.

Substance.	a.	$i = \frac{t}{18{\cdot}5}$.	$i = 1 + (k - 1)a$.
Potassium chloride	0·86	1·82	1·86
Sodium chloride	0·82	1·90	1·82
Lithium chloride	0·75	1·99	1·75
Ammonium chloride	0·84	1·88	1·84
Potassium iodide	0·92	1·90	1·92
Sodium nitrate	0·82	1·82	1·82
Sodium acetate	0·79	1·73	1·79
Potassium formate	0·83	1·90	1·83
Silver nitrate	0·86	1·60	1·86
Potassium sulphate	0·67	2·11	2·33
Potassium oxalate	0·66	2·43	2·32
Barium chloride	0·77	2·63	2·54
Strontium chloride	0·75	2·76	2·50
Lead nitrate	0·54	2·02	2·08
Copper sulphate	0·35	0·97	1·35
Zinc sulphate	0·38	0·98	1·38
Magnesium chloride	0·70	2·64	2·40
Mercuric chloride	0·03	1·11	1·03
Cadmium sulphate	0·35	0·75	1·35

Arrhenius himself remarks that some of these data are not very accurate. Also, in some cases the temperature was not the same in the determinations of the last two columns. Nevertheless, there can be no doubt that a very marked parallelism exists between the figures of the two columns. This shows *a posteriori* that in all probability the assumptions upon which the calculation of these figures is based are in the main correct.

These assumptions—employed by Arrhenius—are:—

1. That van 't Hoff's Law is valid not only for the "majority" of substances, but for *all* substances, even for those which had been previously regarded as exceptions (electrolytes in aqueous solution).

2. That every electrolyte (in aqueous solution) consists partly of "active" molecules (in their electrolytic and chemical bearing) and partly of inactive molecules. These latter as the dilution increases become gradually transformed into active molecules so that at infinitely great dilution only "active" molecules are present.

[Remember that active molecules have no physical existence; they represent the fraction of the molecules which have dissociated into ions.] Arrhenius concludes his paper by answering certain objections to the possibility of electrolytic dissociation.

INFLUENCE OF THE SOLVENT UPON THE MOLECULAR CONDITION OF THE SOLUTE.

Let us take as a typical group of solutes the organic acids and examine their behaviour in various solvents. In benzene solution, and at not too low concentrations, these acids are mainly in the form of double molecules; in ether, ethyl acetate, acetic acid, and similar solvents, they possess their normal molecular weight; when dissolved in water their molecular weights are slightly less than normal, *i.e.* they are slightly electrolytically dissociated. No accurate quantitative result is known in connection with the associating or dissociating power of different solvents. Nernst and Thomson have, however, independently striven to connect the dissociating power of a solvent with its *dielectric constant*, the relation being known as the Nernst-Thomson rule.[1] Water has a high dielectric constant, and is at the same time a remarkably good dissociating solvent. The introduction of a substance of large dielectric constant would certainly tend to weaken the attraction between two oppositely charged electrified particles separated by the substance in question, since the electric force between two charges—suppose they are equal and have the value e—is given by the expression—

$$F = \frac{e^2}{Kr^2}$$

where r is the distance between the charged particles, and K is the dielectric constant. Provided ions were formed at all, therefore, it will be seen that a solvent with large K would tend to cause electrolytic dissociation of the solute to be marked (Nernst even considers that the attractions between *molecules* may be considered in an analogous manner). While the Nernst-Thomson rule holds in many cases, numerous exceptions to it have been discovered, so that it must only be regarded as a qualitative generalisation. The dielectric constant of water is 81 (air = 1), and a few other liquids have also very large dielectric constants, *e.g.* liquid HCN, $K = 95$; H_2O_2, $K = 92{\cdot}8$; formamide, $K = 84$; formic acid, $K = 57$. Ordinary organic solvents have considerably smaller K values. Great dissociation is to be expected on the basis of the Nernst-Thomson rule in the case of the solvents hydrocyanic acid, formamide, and formic acid. Relatively little is known regarding this point, but it appears from the work of Walden (*Trans. Faraday Soc.*, **6**, 71, 1910) that the question is not simply one of the value of the K for the solvent, but likewise depends upon the nature of the solute, *i.e.* whether it be acidic, basic, or neutral. Water is, nevertheless, usually regarded as the typical dissociating solvent.

While this is so, reference ought to be made to some recent investigations by Meldrum and Turner (*Trans. Chem. Soc.*, **97**, 1805, 1910), who, instead of working with acids, bases, and salts have investigated[2] the molecular state of a series of amides in aqueous solution in which it is shown that these bodies are actually associated or polymerised to a certain extent, instead of possessing normal molecular weights as one would expect since they are non-electrolytes.

---

[1] *Zeitsch. physik. Chem.*, 13, 531, 1894.

[2] By the rise of boiling-point method.

The point has been further investigated by Peddle and Turner (*Trans. Chem. Soc.*, **99**, 685, 1911) in the case of certain acids. The authors believe that the apparent association may really be due to dissociation of the solvent molecules, since liquid water is known with considerable certainty to exist partly in the form of $(H_2O)_3$ and $(H_2O)_2$ molecules. Previously evidence had been brought forward by Jones and Getman (*Amer. Chem. Journ.*, **32**, 329, 1904), using the freezing-point method to show that acetic, oxalic, and succinic acids form associated molecules in water. There is no doubt that the question of possible association of solute molecules in water has been somewhat overlooked, but so far no definite conclusion has been reached. It should be pointed out that solutes which contain OH or CN groups are very liable to association when dissolved in organic solvents, especially such solvents as benzene, diphenyl-methane, carbon disulphide, chloroform, and ethylene dibromide, *i.e.* liquids which themselves consist of *un*-polymerised molecules. It is somewhat remarkable that the *polymerisation* of the *solvent* molecules goes hand in hand with their *dissociating power* in respect of solutes dissolved in them, while normality in the *solvent* molecules entails normality or even polymerisation of the *solute* molecules.

FURTHER EVIDENCE FOR THE THEORY OF ELECTROLYTIC DISSOCIATION.

The most general conclusion to be drawn from the theory is that the properties of solutions of electrolytes—say, salts—should be capable of being represented as the *sum* of effects due to the ions, the additivity being more marked the more complete the dissociation, *i.e.* the more dilute the solution. The following illustrates certain properties of solutions from this point of view.

1. We have to deal first with the fact that such solutions conduct current at all, and further Kohlrausch's Law of independent migration of ions, and his expression for equivalent conductivity at infinite dilution. We have already considered this law, *viz.* $\Lambda_\infty = U + V$, where U and V are magnitudes characteristic of the anion and cation respectively, and we have seen that it is very satisfactorily borne out by experiment. The experimental fact that equivalent conductivity increases up to a limit as the dilution increases is the basis of the above expression.

2. *Osmotic Pressure.*—The factor *i*, which may be found, for example, by direct pressure measurement or by freezing-point measurement, is not connected with the specific chemical properties of each acid, base, or salt, but depends essentially on whether the substance is a binary electrolyte (one which can give rise to 2 ions, *e.g.* NaCl, KNO_3), ternary (one which can give rise to 3 ions, *e.g.* Na_2SO_4), quaternary, etc., and also on the particular concentration employed. We have already given a table of values of *i*. It will be seen that at comparable equivalent concentration the osmotic pressures exerted by silver nitrate and sodium chloride are practically identical, being binary

electrolytes (though these substances are very different in their purely chemical effects). Also the ternary electrolytes, sodium sulphate, potassium sulphate, and strontium chloride, exhibit much the same values at comparable concentrations.

3. *Molecular Lowering of Freezing Point and Rise of Boiling Point.*—Closely connected with osmotic phenomena we may similarly group electrolytes as regards the magnitude of their molecular depression of freezing point or elevation of boiling point according as the compounds are binary, ternary, etc. There is again no specific chemical effect characteristic of each individual. The lowering of vapour pressure comes into the same category.

4. *Specific Gravity of Solutions.*—It has been found by experiment that aqueous solutions can be represented fairly closely by an expression such as—

$$\rho = \rho_0 + ac + a_1c^2$$

where ρ = density of the solution;
ρ_0 = „ „ solvent;
c = concentration of solute—say in gram equivalents/liter;
a and a_1 are constants determinable by experiment.

For ordinary purposes it has also been found that this simple expression gives sufficiently close values, *viz.*:—

$$\rho = \rho_0 + ac.$$

Suppose now we have a solution containing two substances, A and B. For solutions which contain A as solute alone the expression holds—

$$\rho = \rho_0 + ac_1$$

and for the solution of B alone—

$$\rho = \rho_0 + \beta c_2$$

then on mixing the two solutes so that the solution is c_1 normal with respect to A, and c_2 normal with respect to B, we get—

$$\rho = \rho_0 + ac_1 + \beta c_2.$$

Now if we assume electrolytic dissociation to be true, and take a very dilute solution of a salt which is presumably practically completely dissociated, *e.g.* sodium chloride into sodium ions and chlorine ions, we may look upon these ions as corresponding to the two substances A and B, always present, however, in equivalent concentration. Now let us suppose we had four solutions, *viz.* a solution of sodium chloride, possessing a density value ρNaCl, sodium bromide, density ρNaBr; ammonium chloride, ρNH_4Cl; ammonium bromide, ρNH_4Br. Further, let a be the coefficient (in the density expression) for $Na^{\cdot}$ ion; and similarly let β refer to Cl' ion; γ to Br' ion; δ to $NH_4^{\cdot}$ ion.

Then if we take as a special case 0·1 normal solution of these four salts, we have the relations (ρ_0 = 1)—

$$\rho\text{NaCl} = 1 + 0{\cdot}1\,(\alpha + \beta)$$
$$\rho\text{NaBr} = 1 + 0{\cdot}1\,(\alpha + \gamma)$$
$$\rho\text{NH}_4\text{Cl} = 1 + 0{\cdot}1\,(\delta + \beta)$$
$$\rho\text{NH}_4\text{Br} = 1 + 0{\cdot}1\,(\delta + \gamma)$$

and consequently—

$$\rho\text{NaCl} - \rho\text{NaBr} = \rho\text{NH}_4\text{Cl} - \rho\text{NH}_4\text{Br},$$

that is, provided we are dealing with an additive property—the above equations being a typical way of expressing such a state of things. Experiment (*e.g.* Valson, *C. R.*, **73**, 441, 1871; **77**, 806, 1873) has shown the above expression to be in accordance with fact, and hence we have support for the dissociation theory, since it likewise requires the property in great dilution to be an additive one.

5. *Optical Refractivity of Solutions.*—The refractive index of the solvent—water—is first determined. It is then found possible by a suitable choice of moduli or coefficients which are supposed to be characteristic of the ions, to calculate what the refractive index would be for a solution of any given concentration. Experiment goes to show that the property is an additive one, the agreement between calculated values and those experimentally obtained being moderately good.

6. *Optical Activity or Natural Rotatory Power of Solutions.*—Some organic compounds are capable of rotating the plane of polarisation of light passed through them. If therefore a series of salts containing an optically active anion and inactive cations be examined, then equivalent quantities of all the salts should have equal rotatory power, if the dilution is sufficiently great to allow dissociation to be practically complete. This has been confirmed, for example, in the case of the salts of quinic acid, the anion of which salts is active. A series of $\frac{N}{7}$ solutions[1] give the following molecular rotations:—

Potassium quinate,	48·8	Barium quinate,	46·6
Sodium „	48·9	Strontium „	48·7
Ammonium „	47·9	Magnesium „	47·8

It should be noted particularly that the molecular rotation of the active *free acid* itself—not the anion—is 43·4, a number which differs from the constant value obtained for the salts.

Quite similar results are obtained with the camphorates (*i.e.* Na, K, Li, Ba, Ca, Mg, NH_4 camphorates). It has been observed that as we increase the dilution, the molecular rotatory power of all these salts tends to the same constant limit, namely 39°. This relation is known as Oudemann's Law. The value found for *free* camphoric acid in dilute solution is a quite different matter, however, namely, 93°. It is, therefore, impossible to try and explain the convergence of the values for the salts as being due to the progressive dissociation into acid and base (as used to be believed), for if so one would expect to reach the value 93°, since the base is quite inactive. The fact that we reach quite a different value, *viz.* 39°, is extremely strong evidence in favour of the electrolytic dissociation theory, for according to this, dissociation does *not* take place into acid and base, but into electrically charged cation and anion. The value 39°, therefore, is due to the *ion* of camphoric acid, whilst 93° is due to the molecule of camphoric acid, since camphoric acid is scarcely dissociated at all. The theory thus affords a very satisfactory explanation of Oudemann's Law.

---

[1] A better test of the theory would have been afforded had these solutions been much more dilute.

7. *Absorption Spectra of Solutions.*—When one passes a beam of white light through a prism so as to spread it out into a spectrum containing all the colours continuously from red to violet, it has been found that by interposing a vessel containing a solution, it very frequently happens that certain of the colours are now absent, *i.e.* have been absorbed by the solution. This naturally must occur with coloured solutions, since the colour is due to absorption, though it should also be remembered that what we call colourless solutions may also show absorption for different wave-lengths other than those contained in the relatively short range which the eye can detect, and which we call the visible spectrum. At present, however, we are considering visibly coloured solutions. A very striking confirmation of the electrolytic dissociation theory was afforded by the work of Ostwald (*Zeitsch. physik. Chem.*, **9**, 579, 1892) on the permanganates in aqueous solution. By photographing the spectrum thus produced, on the same plate, one obtains spectral images of different solutions, which contain the same coloured anion in equivalent quantities with various cations. A number of absorption bands were produced by the interposition of the solutes, and the important point is that when the solutions were dilute 0·002 N, the bands for each salt (*e.g.* sodium permanganate, potassium permanganate, ammonium permanganate, etc.) fell at exactly the same place. The spectrum was independent of the nature of the cation, except in a few cases where deviations occurred, and could be attributed to disturbing secondary effects. The identity of the spectra could be expected from the theory of free ions.

It should be pointed out, however, that Ostwald's conclusion in this connection has been recently criticised by Merton,[1] who photographed the absorption spectra of various permanganates in various solvents. He found that the position of bands in any single solvent is the same for permanganates of potassium, sodium, calcium, barium, zinc, etc., and he therefore suggests—since some of the solvents employed could only possess very slight ionising power—that the absorption is due to the MnO_4 group, and is not much influenced by ionisation. Chemical reaction between the solvents and the solutes prevented determinations of concentration. Naturally, if Merton's view is correct as regards the unimportance of dissociation, it is clear that Ostwald's results cannot be urged as positive evidence in favour of the electrolytic dissociation theory. [For a very complete discussion of optical properties from the chemical standpoint, the reader is referred to E. C. C. Baly's *Spectroscopy* (Sir William Ramsay's series of textbooks).]

---

[1] *Trans. Chem. Soc.*, **99**, 637, 1911.

In connection with the phenomena of colour it should be mentioned that the application of indicators in acidimetry and alkalimetry is based upon the colour changes involved (directly or more probably indirectly) in passing from the undissociated to the dissociated state, or *vice versâ*, or rather the theory of electrolytic dissociation has been shown to give a rational explanation of the reactions referred to.

8. *Specific Catalytic Effects attributed to Ions.*—It has been observed that many reactions in solution take place very slowly if the substance, or substances are alone present in the solvent, while the rate of reaction is increased by the addition of certain substances which apparently take no definite stoicheiometric part, *i.e.* they do not appear in the ordinary form of writing the reaction equation. This action, which apparently is merely due to the presence of the substance, is called catalysis, the accelerating substance being called a catalyser or catalyst. There are two sorts of catalysis—homogeneous and heterogeneous. We are only dealing with homogeneous at present, *i.e.* the catalysis due to some substance which itself dissolves in the solution in which the reaction is taking place. The typical example of a reaction which can be catalysed is the conversion of cane sugar into dextrose and lævulose in aqueous solution. At ordinary temperatures this takes place very slowly, the reaction equation being—

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

When, however, we add acids such as HCl, HNO_3, H_2SO_4, the reaction goes much faster and, further, the speed depends on the concentration of the catalyst. For dilute solutions of the acid the reaction velocity is practically proportional to the equivalent conductivity of the acid (Ostwald, *J. prakt. Chem.*, **28**, 449, 1883; **29**, 385, 1884; **30**, 93, 1884). Now the only thing these and other acids have in common is the H atom, which on the electrolytic dissociation theory becomes $H^\cdot$ ion, and the catalysis is considered to be due to this. Further, on the theory the concentration of the $H^\cdot$ ion is the ratio $\frac{\Lambda_v}{\Lambda_\infty}$, and since Λ_∞, as shown by Kohlrausch, has very much the same value for all acids, it would follow that the relative catalytic effect of different acids should be proportional to the equivalent conductivity.

Ostwald obtained the numbers given in the following table for Λ and k_1 (the velocity of inversion of the sugar). [We shall study velocity of reactions later on by themselves, and see then the exact meaning of k_1.] The equivalent conductivity of HCl (in 1 normal solution) is set equal to 100 (though this is not its value when expressed in the usual units); and the velocity of inversion, caused by the same acid (in 0·5 N solution) is also set equal to 100.

Acid.	Λ.	k_1.	k_2.
HCl.	100	100	100
HNO_3	100	100	92
H_2SO_4	59·5	54	55
Trichloracetic . . .	—	75	68
Dichloracetic . . .	33·0	27·1	23
Monochloracetic . .	6·41	4·84	4·3
Acetic	0·67	0·4	0·34

The values denoted by k_2 are the velocities of saponification of an ester in presence of 0·67 normal solutions of the acids mentioned. There is a marked parallelism in the values for the velocities and equivalent conductivities. More accurate determinations were carried out later by Arrhenius (*Zeitsch. physik. Chem.*, **4**, 244, 1889) and Palmaer (*Zeitsch. physik. Chem.*, **22**, 492, 1894). This work showed that at a high dilution the velocity of inversion and the fraction of the acid dissociated are directly proportional. The above effects are considered as due to the $H^{\cdot}$ ions. We likewise have examples of catalytic effects due to other ions, *e.g.* OH' ions.

9. *Mixtures of Salts in Solution.*—A striking fact in connection with the chemical properties of salts in solution is that the acidic and basic portions generally exhibit exactly the same reactions, independent of the particular salt of which they originally formed the constituents. Thus, *all* soluble barium salts give with all soluble sulphates exactly the same reaction, namely, the formation of barium sulphate. Similarly, $AgNO_3$ will form a precipitate of AgCl by interaction with any soluble chloride, KCl, NaCl, $CuCl_2$, $BaCl_2$, etc. This is quite characteristic of inorganic salts in aqueous solution, so much so that it has been found possible to draw up a scheme of analysis whereby the constituents of a solution may be detected and recognised simply by applying this conception of the specific effect of each constituent. It will be obvious how simply this is explained on the assumption of free ions. Our systems of qualitative and quantitative analyses are based essentially on reactions of ions. There are cases, however, which appear to contradict these simple statements. Take, for example, a silver salt and add KCN solution. At first a white precipitate is formed which redissolves on adding excess of KCN, and this solution no longer gives the ordinary reaction for silver (ion), say, on adding KCl. It has long been assumed that a complex was formed, and by introducing this idea into the ionic theory we arrive at the concept of a complex ion. Migration experiments, *i.e.* measurements of the motion of ions in an electric field, have conclusively shown that such ionic complexes do actually exist. In the particular case cited it has been shown that the *direction* in which the silver has moved (by ultimately analysing the liquid at different places) is toward the anode (the + pole). The silver must therefore be present as a complex anion instead of in its ordinary state as $Ag^{\cdot}$ cation. As a matter of fact,

experience has shown that in excess KCN solution the silver is present as the anion $(AgCN_2)'$, the cation being $K^{\cdot}$. This explains the absence of the ordinary reactions due to $Ag^{\cdot}$, for this no longer exists in appreciable amount in the solution. Similar instances occur when AgCl is dissolved in NH_3; when NH_3 is added to solutions of copper salts; and when mercuric iodide HgI_2 is dissolved in KI solution. The idea of simple ions and complex ions has been found sufficient to afford an explanation for all the reactions of aqueous solutions. In the case of organic bodies in solution, however, we generally find these to be non-electrolytes. We therefore assume that no ions are present; and hence any system of analysis of organic substances in solution comparable with our systems of inorganic analysis is impossible.

A question which has frequently arisen is—What happens when two salts, say K_2CO_3 and Na_2SO_4, are mixed together in aqueous solution? According to the electrolytic dissociation theory, these salts would be very largely split up into their ions. That is to say, the solution would contain on the simplest assumptions, $Na^{\cdot}$, $K^{\cdot}$, CO_3'', SO_4'', and it is clear that it is quite impossible to tell to what salt these ions originally belonged, for in the solution they have become independent of the constituent originally combined with them. The dissociation theory is thus in good agreement with these observations. A further point to notice is that the dissociation takes place with immeasurably rapid velocity, *i.e.* it is instantaneous to all intents and purposes.

10. *Physiological Action of the Ions.*—This has been developed to a very great extent recently, notably by Arrhenius in his *Immuno Chemistry*. We shall only consider a single illustration—the poisonous property. The results of investigation showed that all potassium salts have nearly the same poisonous effect in solutions of equal concentration. This, of course, does not hold when the anion is likewise poisonous, as in the case of KCN. Kahlenberg (*Journal Physical Chemistry*, **4**, 553, 1900), and Loeb (*Pflüger's Archiv*, **69**, 1897; **71**, 457, 1898), as well as Paul and Krönig (*Zeitsch. physik. Chem.*, **21**, 414, 1897), have investigated the action of salts on bacteria and spores, and the results are in general what would be expected on the basis of the dissociation theory.

11. *Heat of Neutralisation of Acids and Bases.*—The reaction in a typical case of neutralisation is usually represented thus—

$$HCl + NaOH = NaCl + H_2O.$$

According to the dissociation theory (assuming it to be true), when we add acid to the base we have in solution the following ionic reaction:—

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + HOH.$$

It will be noted that we have not written $H^{\cdot} + OH'$ in the last term. We know from conductivity experiments that water is almost a non-conductor, that is to say, the quantity of $H^{\cdot}$ and OH' present is extremely small.

When neutralisation occurs, therefore, practically all the $H^{\cdot}$ and OH'

unite to form undissociated water. But it will be noticed in the above ionic reaction that $Na^{\cdot}$ and Cl' appear in exactly the same condition on both sides of the equation. Eliminating these common terms, we get as the nucleus of the total reaction—

$$H^{\cdot} + OH' \rightarrow H_2O.$$

The heat of neutralisation of a practically completely dissociated acid with a similarly dissociated base is simply due to the formation of water from its ions. For all strong acids and bases the heat should, therefore, be the same for the same amount of water formed. This has been found to be the case, *viz.* approximately 137 centuple calories (1 centuple calorie = 100 gram-calories) per gram-molecule of water produced. Dilute solutions of the following acids were neutralised with caustic soda also in dilute solution :—

	Heat of neutralisation.
HCl	137 centuple calories, K
HBr	137 ,, ,,
HI	137 ,, ,,
$HClO_3$	138 ,, ,,
$HBrO_3$	138 ,, ,,
HIO_3	138 ,, ,,
HNO_3	137 ,, ,,

A similar table for the heat of neutralisation of strong bases by a strong acid (HCl) is given :—

	Heat of neutralisation.
Li hydroxide	138 centuple calories, K
Na ,,	137 ,, ,,
K ,,	137 ,, ,,
Tl ,,	138 ,, ,,
Ba ,,	139 ,, ,,
Sr ,,	138 ,, ,,
Ca ,,	139 ,, ,,
Tetramethylammonium hydroxide	137 ,, ,,

When, however, we work with weaker acids or bases, *i.e.* those which are not completely (or nearly completely) dissociated at the dilutions employed, the results are different. It seems reasonable to ascribe this to the (positive or negative) heat of *dissociation* of the weak acid or base. Using caustic soda as base (practically completely dissociated) and neutralising with weak acids, the following results were obtained :—

Metaphosphoric	143 K
Hydrofluoric	163 K
Acetic	134 K

while for weak bases neutralised by the strong acid HCl, the following figures have been obtained :—

Ammonia (ammonium hydroxide)	122 K
Methylammonium hydroxide	131 K
Diethylammonium hydroxide	118 K
Triethylammonium hydroxide	87 K

Note that some of these numbers are above 137 K, some below. As regards the reaction here occurring, the weak acid or base must dissociate more and more in order to keep itself in equilibrium with its ions, one of which is disappearing to give H_2O. We might look upon the process as first of all involving a dissociation of the weak acid or base, and this means a heat effect. Also it is important to remember that salts containing a weak acid or base, or both, suffer more or less extensive hydrolytic decomposition owing to action of the water (the solvent), *e.g.* sodium acetate in water undergoes a partial decomposition according to the equation—

$$CH_3COONa + H_2O = CH_3COOH + NaOH.$$

Thus we find a little free acetic acid and free alkali in the solution. Owing to the dissociation of acetic acid being extremely small, and that of caustic soda being practically complete, the result is that the solution reacts alkaline. Alkalinity or acidity is very characteristic of hydrolysis, but we shall not consider the point at this stage. The important thing for the present to note is that we can have acetic acid and alkali coexisting (to a small extent) without further formation of salt, *i.e.* the neutralisation process which occurs when we add NaOH to acetic acid does not go quite completely, and hence, owing to this cause, there is not the normal heat evolution of 137 K per equivalent but something less than this. The effect here considered is in general very small, indeed negligible in most cases. The theory of free ions affords the best explanation we have yet got for both the normal values and the abnormal. It may be mentioned that from electromotive force measurements the heat evolved in H_2O formation can be even calculated and comes out about 137 K.

12. *Evidence from the Measurements of Electromotive Force of Cells.* —The great advances which, since 1888, have been made in the study of the electromotive force, and especially the conception or a "reversible electrode," could not have been rendered possible without the dissociation theory.[1] The evidence of these phenomena must, however, be postponed until we are in a position to consider the matter from the standpoint of thermodynamics.

It has been claimed more than once that the abnormal osmotic pressures exhibited by strong electrolytes can be explained by the hypothesis of a hydrolytic decomposition into acid and base, for instance—

$$NaCl + H_2O = NaOH + HCl.$$

---

[1] Especially results such as those obtained from gravity and centrifugal cells. *Cf.* Tolman, *Proc. Amer. Acad.*, Sept., 1910.

This assumption is shown to be quite inadequate, in the first place, by the fact that the acid and base which in their turn *cannot* undergo a hydrolytic change of the above nature also show, like the salt, abnormal osmotic pressures; secondly, if the above were true, the heat of neutralisation should not be a constant quantity for strong acids and bases, nor should it come out to be (as it is) identical with the heat of formation of water; thirdly, results such as those of Oudemann on the optical rotary power of salt solutions (say, of camphoric acid), at great dilution, in which the limiting value for the rotation differed quite markedly from that of the free acid, contradict any such hypothesis. The conception of free ions, however, affords, as already shown, very satisfactory explanation of all these phenomena.

Having now reasonably established the *existence* of ions, we may go on to study some of the consequences of the electrolytic dissociation theory. Let us first of all consider the motion of the ions in an electric field.

SOME CONSEQUENCES OF THE ELECTROLYTIC DISSOCIATION THEORY. THE "MOBILITY" OF THE IONS AND THEIR ABSOLUTE VELOCITIES UNDER A GIVEN POTENTIAL GRADIENT.

We have already discussed (p. 191) the generalisation known as Kohlrausch's Law, namely, that the equivalent conductivity, say of a binary electrolyte such as KCl, at infinite dilution (*i.e.* at a dilution so great that dissociation is complete) may be represented as the sum of two independent quantities called the mobility of the cation and anion respectively—

$$\Lambda_\infty = U_c + V_a.$$

We have likewise shown that (p. 194)—

$$\Lambda_\infty = F(u_c + v_a)$$

where F = one Faraday = 96540 coulombs.
u_c and v_a = absolute velocity in cms. per second of each ion under a potential gradient of 1 volt per centimetre.

Hence it follows that—

$$\begin{aligned} U_c &= Fu_c \\ V_a &= Fv_a \end{aligned} \quad \text{and} \quad \frac{U_c}{V_a} = \frac{u_c}{v_a}.$$

If we could measure U_c or V_a, we could calculate u_c or v_a, and *vice versâ*; and having got one of these quantities, we could apply Kohlrausch's Law to get the corresponding values of any other ion.

We shall first of all deal with the work of Hittorf who measured the *ratio* $\frac{U_c}{V_a}\left(\text{or } \frac{u_c}{v_a}\right)$ for several cases. If we increase the fraction $\frac{U_c}{V_a}$ by unity, we get $\frac{U_c + V_a}{V_a}$, and to the reciprocal of this expression, *viz.* $\frac{V_a}{U_c + V_a}\left(\text{or } \frac{v_a}{u_c + v_a}\right)$, Hittorf gave the name "*Transport number of the* *anion*". To the corresponding expression, $\dfrac{U_c}{U_c + V_a} \left(\text{or } \dfrac{u_c}{u_c + v_a}\right)$, he gave the name "*Transport number of the cation*". His method of measurement of transport numbers consisted essentially in allowing a known quantity of electricity to flow for a time through the solution in question. He then analysed the liquid in the region of the anode and cathode, and determined the change in concentration of the corresponding ions, which had taken place owing to the wandering of the ions during the electrolysis. If the transport number for, say, the cation of any given salt were to come out unity, it would mean that the entire current had been carried by this ion. This is quite an imaginary case, since it would require one of the ions to move infinitely slowly compared with the other under the same conditions as regards electric field. The transport number 0·5, which is what one finds nearly reached in many cases, would mean that half the current is carried by the cations, half by the anions. The most exact measurements of transport numbers yet made refer to KCl, which give 0·497 for the K˙ cation at 18° C. We may therefore regard the transport number, say, of the cation, either as the ratio of its velocity to the sum of the absolute velocities of anion and cation, or as the ratio of the mobility of the cation to the sum of the mobilities of cation and anion, or as the fraction of the total current carried by the cation, for evidently the greater the mobility or velocity, the greater the number of coulombs transferred in a given time, and if we introduce a proportionality factor to indicate the connection between the two quantities, it will be seen that the factor vanishes in the ratio $\dfrac{U_c}{U_c + V_a}$, the sum $U_c + V_a$ being proportional to total current, and U_c proportional to the fraction carried by the cation.[1]

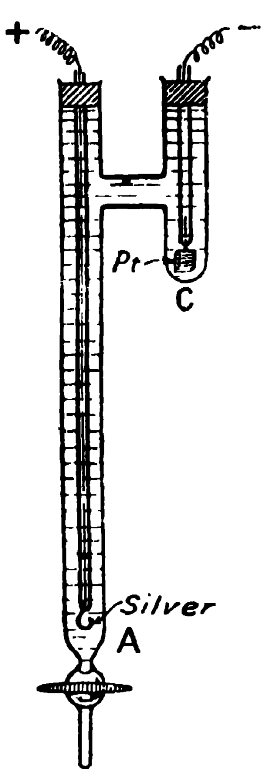


FIG. 44.—Apparatus for measuring the Transport Number of the Silver ion in Silver Nitrate solution.

A very simple type of apparatus for measuring transport numbers is shown in Fig. 44. A is an electrode of silver, C an electrode of platinum or silver. The vessel is supposed completely filled with silver nitrate solution, and current is passed through the cell from left to right. The Ag ion moves from left to right towards the cathode C. The

---

[1] The mechanism of current conduction and the movement of the ions is considered in some detail in a paper by S. W. J. Smith, *Proc. Phys. Soc.*, 28, Part III. 148 (1916).

NO'_3 ions move in the opposite direction. Q units of electricity pass through the cell, this current being measured by means of a copper voltameter placed in circuit. Silver dissolves off A corresponding to the quantity of electricity Q. If the $Ag^{\cdot}$ ions did not move at all, the solution in the long limb would have increased in $Ag^{\cdot}$ ion concentration by an amount electrochemically equivalent to Q. But since $Ag^{\cdot}$ ion *does* move, it will be found by analysis of the contents of the anode compartment that the increase in the mass of silver (in the ionic form, of course) is not as great as that which corresponds to Q. The difference between the mass of silver which should have been finally present in the compartment had no movement of the $Ag^{\cdot}$ ion taken place, and the mass actually present represents the quantity transported. This mass of silver divided by the mass of silver which corresponds to Q, is the transport number of the silver ion.[1] This quantity subtracted from unity gives at once the transport number for the anion. At ordinary temperatures the transport number of $Ag^{\cdot}$ is not very different from that of NO'_3, the latter being the greater of the two.

We may now advance a step further by combining the transport number $\frac{U_c}{U_c + V_a}$ with the equivalent conductivity at infinite dilution, taking Kohlrausch's Law into consideration. Thus, in the particular case of potassium chloride, experiment shows that at 18° C. the transport number of the cation, *viz.*—

$$\frac{U_c}{U_c + V_a} = 0{\cdot}497.$$

Also $\Lambda_\infty = 130{\cdot}1$ (the units being the reciprocal ohm and concentration in equivalents per c.c.)

$$= U_c + V_a.$$

Hence
$$\frac{U_c}{130{\cdot}1} = 0{\cdot}497,$$

and hence $U_c = 64{\cdot}67$ under a gradient of 1 volt per cm. By subtraction one finds $V_a = 65{\cdot}44$ under the same gradient.

Further, these mobility terms are connected with the absolute velocity of the ions (under unit potential gradient) by the relation $U_c = Fu_c$; $V_a = Fv_a$. Therefore, in the above case, since F is always 96,540 coulombs, it follows that the absolute velocity u_c of the cation under a potential gradient of 1 volt per cm. is $6{\cdot}7 \times 10^{-4}$ cms. per sec., the corresponding value for the anion v_a being $6{\cdot}78 \times 10^{-4}$ cms. per sec. It will be observed that the ions under unit gradient move very slowly. In the following table are given the values of the mobility and absolute velocity of a number of ions in aqueous solution at 18° C., under a potential gradient of 1 volt per cm. It will be observed that $H^{\cdot}$ ion is the most rapidly moving ion, OH' coming next at about one-half the value of the $H^{\cdot}$ ion.

---

[1] For a concrete case showing the details of calculation, the reader should consult a textbook of practical physical chemistry, *e.g.* Findlay's *Practical Physical Chemistry.*

Ion.	Temperature 18° C. Absolute Velocity in cms. per Second.	Mobility.
$H^{\cdot}$	$32·50 \times 10^{-4}$	318
$K^{\cdot}$	6·70 ,,	64·67
$Na^{\cdot}$	4·51 ,,	43·55
$Li^{\cdot}$	3·47 ,,	33·44
$Ag^{\cdot}$	5·70 ,,	54·02
OH' . . .	17·80 ,,	174
Cl'	6·78 ,,	65·44
NO_3' . . .	6·40 ,,	61·78
CH_3COO' . .	3·20 ,,	35

NOTE.—At 25° C. the most probable value for the mobility of $H^{\cdot}$ ion in very dilute aqueous solution is 347·2 (*cf.* Kendall, *Trans. Chem. Soc.*, **101**, 1283, 1912).

One can see, therefore, that the equivalent conductivity at infinite dilution of *acids* must be greater than bases, and these greater again than salts under the same condition. Of course this is arguing backwards, for it is from the value of Λ_∞ that the mobility and velocity values are obtained as a rule. Besides this indirect method, however, we are indebted to Lodge for the first *direct* determination of the absolute velocity of $H^{\cdot}$ ion (*Brit. Assoc. Rep.*, 1886, p. 389). The apparatus is represented diagrammatically in Fig. 45.

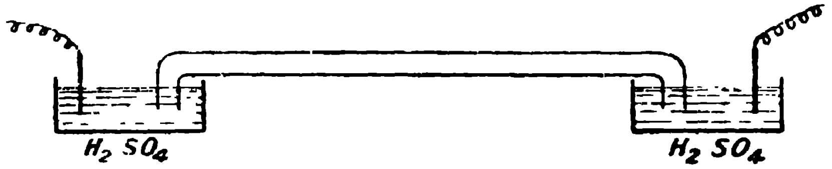


FIG. 45.

The horizontal tube contains set gelatine impregnated with a little phenolphthalein and sodium chloride, to which has been added a trace of NaOH, just sufficient to colour the phenolphthalein red. When current is passed, $H^{\cdot}$ ions from the acid move in a certain direction, decolorising the jelly tube as they move, and by reading the shift of the colour boundary at certain time intervals, the velocity of the $H^{\cdot}$ ion is got directly for the particular potential applied between the electrodes. One can easily calculate from this the velocity under 1 volt per cm. Lodge's first experiment gave the result 29×10^{-4} cms. per second under 1 volt per cm.; later experiments gave 26×10^{-4} and 24×10^{-4} respectively. It will be seen that these—especially the first—are in fairly good agreement with Kohlrausch's indirectly-found value 32×10^{-4}. Lodge also employed the gelatine tube method for other ions. He found, for example, that SO_4'' travels at about one-third the speed of $H^{\cdot}$ ion.

At a later date Whetham[1] introduced a modification of Lodge's method which is applicable to *coloured* ions, say, cupric ion $Cu^{\cdot\cdot}$ in copper sulphate solution. Above the layer of copper sulphate solution there was carefully poured a colourless solution of a salt with the same anion, having the same specific conductivity as the copper salt, this being necessary to keep the potential gradient the same along the tube. On applying the potential in the proper direction, the $Cu^{\cdot\cdot}$ ions moved into the colourless solution so that the position of the surface of demarcation moved, and the extent of this movement in a given time could be measured. This "moving boundary method" was further extended notably by Steele[2] to colourless solutions, the movement of the boundary being measured by the change in refractive index which occurs as the boundary passes through the field of vision of a refractometer. A source of error in this type of measurement due to the movement of the solvent itself along the walls of the tube, a process known as "cataphoresis" or "electrical endosmose," was pointed out by Abegg and Gaus,[3] who also showed how this could be corrected for. This work was extended by Dennison,[4] whose paper should be consulted as well as that of Lash Miller.[5] G. N. Lewis (*Journ. Amer. Chem. Soc.*, **32**, 863, 1910) has pointed out the necessity of correcting the distance through which the boundary moves for any displacement of the liquid caused by electrode effects. Miller (*loc. cit.*) and Lewis (*loc. cit.*) have further shown that, when thus corrected, the moving boundary method gives a quantity identical with that obtained by the Hittorf method. We may refer to this quantity as the Hittorf Transport Number.

In addition to the methods already mentioned, another has been developed by Washburn (*Technological Quarterly*, p. 386, 1908; also *Journ. Amer. Chem. Soc.*, **37**, 698, 1915). This method depends upon the use of a reference substance, a non-electrolyte such as sugar, which remains stationary during the passage of the current. The necessity for introducing such a substance is as follows. In the Hittorf method it is assumed that the water itself is stationary. If, however, the ions are hydrated, and this appears to be generally the case, their movement will involve the transport of water owing to this cause. This movement of the water will not be the same in both directions, for it is unlikely that the anion and cation would be hydrated to an extent that just left the water concentration virtually unaltered. The net result is that water accumulates in one compartment, and hence, since the concentration of the ion is referred to the quantity of water present, a slightly erroneous value for the actual *change* in concentration of the ion—as a result of the passage of the current—is obtained. Using a substance such as sugar, which is assumed to be really stationary, one can readily observe, say by means of a polarimeter, the *apparent* change in the sugar concentration which has been caused by the drift of the water accompanying the migrating ions (as water of hydration). In this way the correct change in the concentration of the ion (referred to the water) may be calculated. The resulting value is known as the True Transport Number of the ion considered. In very dilute solutions the Hittorf Transport Number and the True Transport Number are practically identical.

---

[1] *Phil. Trans.*, 337, **A**, 1893; 507, **A**, 1895.

[2] *Ibid.*, **198**, **A**, 105, 1902; *Zeitsch. physik. Chem.*, **40**, 689, 1902.

[3] *Zeitsch. physik. Chem.*, **40**, 737, 1902.

[4] *Ibid.*, **44**, 575, 1903.

[5] *Ibid.*, **69**, 436, 1909.

Washburn (*Journ. Amer. Chem.*, *loc. cit.*) has shown that this method likewise gives us the *relative* degree of hydration of the various ions. In the table below are given some of Washburn's values for the True Transport Numbers of the cations in the following salts:—

Electrolyte Concentration = 1·3 normal.	Hittorf Transport No.	True Transport No.	Transport No. at Infinite Dilution.
HCl . . .	0·82	0·844	0·833
CsCl . . .	0·485	0·491	0·491
KCl . . .	0·482	0·495	0·495
NaCl . . .	0·366	0·383	0·396
LiCl . . .	0·278	0·304	0·330

The Hittorf Numbers and the True Numbers quoted above refer to the concentration 1·3 normal of the salt. It will be observed that concentration has a slight effect upon the Transport Number. The Transport Number also varies somewhat with the temperature. As the temperature increases all the Transport Numbers so far measured tend to approach the value 0·5. This means that at high temperatures each ion tends to carry the same fraction, one-half of the current.

Of course the validity of the reference-substance method depends upon the assumption that the reference substance is really stationary. In the case of solutions of hydrochloric acid there is evidence that sucrose combines with the $H^{\cdot}$ ion to a certain extent and will therefore move with this ion, so that sucrose could not be employed justifiably with this electrolyte. With KCl and other salts sucrose appears to be stationary. With a suitable choice of reference substance this method is the most satisfactory one yet proposed.

EXAMPLES OF THE EXTENT OF ELECTROLYTIC DISSOCIATION.

It has already been shown that the degree of dissociation or ionisation, α, can be obtained from the expression $\alpha = \Lambda_v/\Lambda_\infty$. The validity of this expression depends upon the supposition that the mobilities of the ions do not vary with the concentration. It is known, however, that aqueous solutions of acids, bases, and salts at moderate concentrations exhibit a viscosity or internal friction which is slightly different from that of pure water. In some cases the solution has a smaller viscosity than that of the solvent, but in the majority of cases a greater viscosity. Since this means that there is a change in the resistance to the movement of the particles through the liquid, it is to be anticipated that the mobility, and therefore the conductivity, of an ion will decrease (increase) at least approximately in the same proportion in which the viscosity increases (decreases). This was first suggested by Arrhenius (*Zeitsch. phys. Chem.*, **9**, 495, 1892). To allow for this effect, it is necessary to reduce the observed conductivity to the value which it would possess if the viscosity of the solution were identical with that of the solvent. This correction is carried out by writing—

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} \cdot \frac{\eta_v}{\eta_o}$$

where η_o is the viscosity of the solvent, η_v the viscosity of the solution under examination. It is convenient to take the viscosity of the medium as unity, and express η_v in terms of this unit. As a matter of fact this correction is usually small, and in many cases negligible, when the concentration of the solute does not exceed 0·5 normal. Thus, up to this limit, solutions of NaCl, KCl, and many other salts do not exhibit any very sensible change in the value of α when the viscosity correction has been applied. A few salts, however, are characterised by possessing higher viscosity in solution than the majority. Such a salt is lithium chloride. This salt is therefore to be regarded as rather an extreme case. The magnitude of the correction will therefore be appreciated by comparing the values of α corrected and uncorrected in the case of aqueous solutions of this salt.

LITHIUM CHLORIDE AT 18° C.

Concentration of Salt in Equivalents per Liter.	Λ_v/Λ_∞.	$\frac{\Lambda_v}{\Lambda_\infty} \cdot \frac{\eta_v}{\eta_0}$.
0·5	0·715	0·766
0·2	0·787	0·812
0·1	0·833	0·846
0·05	0·870	0·878
0·01	0·931	0·932

Naturally the application of the viscosity correction requires some justification. "This is most clearly shown in the case of temperature, the effects of which on the viscosity of water and on the mobility of ions in dilute aqueous solution are approximately the same" (Noyes and Falk, *Journ. Amer. Chem. Soc.*, **34**, 454, 1912). This was first pointed out by Kohlrausch (*Proc. Roy. Soc.*, **71**, 383, 1903).

The form of the viscosity correction has been discussed by Washburn (*Journ. Amer. Chem. Soc.*, **33**, 1464, 1911), who suggests, in place of the simple proportionality correction, the slightly modified and at the same time wholly empirical form—

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} \cdot \left(\frac{\eta_v}{\eta_o}\right)^m$$

where m never differs from unity by more than 0·2. For all general purposes the simple corrected formula is sufficiently exact.

We may now give some examples of the extent of ionisation as measured by the conductivity-viscosity expression of Arrhenius—

$$a = \frac{\Lambda_v}{\Lambda_\infty} \cdot \frac{\eta_v}{\eta_0}.$$

A. *Strong Electrolytes* (good conductors of electricity).

Noyes and Falk (*loc. cit.*) have made a valuable compilation of the most accurate data available (up to 1912) of the equivalent conductivities of a large number of acids, bases, and salts. The following examples are taken from their tables. The data refer to the temperature 18° C.

SODIUM CHLORIDE.

Concentration in Equivalents per Liter.	Λ_v.	η_v/η_0.	$\Lambda_v \eta_v/\eta_0$.	$a=\frac{\Lambda_v}{\Lambda_\infty}\cdot\frac{\eta_v}{\eta_0}$.
1·0	74·31	1·086	80·7	0·741
0·5	80·89	1·041	84·21	0·773
0·2	87·67	1·0167	89·13	0·818
0·1	91·96	1·0086	92·75	0·852
0·05	95·66	1·0046	96·10	0·882
0·02	99·55	1·0018	99·73	0·916
0·01	101·88	1·0009	101·97	0·936
0·005	103·71	unity	103·71	0·953
0·002	105·48	"	105·48	0·969
0·001	106·42	"	106·42	0·977
0·0005	107·11	"	107·11	—
0·0002	107·75	"	107·75	—
0·0001	108·03	"	108·03	—
0·0000[1]	108·9 $= \Lambda_\infty$	"	108·9	1·000

POTASSIUM CHLORIDE.

Concentration in Equivalents per Liter.	Λ_v.	η_v/η_0.	$\Lambda_v \eta_v/\eta_0$.	$a=\Lambda_v\eta_v/\Lambda_\infty\eta_0$.
1·0	98·22	0·982	96·5	0·742
0·5	102·36	0·9898	101·3	0·779
0·2	107·90	0·9959	107·5	0·827
0·1	111·97	0·9982	111·8	0·860
0·05	115·69	0·9991	115·6	0·889
0·02	119·90	0·9996	119·9	0·922
0·01	122·37	unity	122·37	0·941
0·005	124·34	"	124·34	0·956
0·002	126·24	"	126·24	0·971
0·001	127·27	"	127·27	0·979
0·0005	128·04	"	128·04	—
0·0002	128·70	"	128·70	—
0·0001	129·00	"	129·00	—
0·0000	130·0 $= \Lambda_\infty$	"	130·0	1·000

---

[1] Naturally the zero here does not actually mean total absence of salt; it means a concentration less even than 0·0001 normal.

SILVER NITRATE.

Concentration in Equivalents per Liter.	Λv.	η_v/η_0.	$\Lambda v\ \eta_v/\eta_0$.	$a = \frac{\Lambda_v}{\Lambda_\infty}\frac{\eta_v}{\eta_0}$.
1·0	67·6	1·057	71·5	0·617
0·5	77·5	1·020	79·1	0·683
0·2	—	—	—	—
0·1	94·33	unity	94·33	0·814
0·05	99·50	,,	99·50	0·859
0·02	105·1	,,	105·1	0·908
0·01	107·80	,,	107·80	0·931
0·005	110·03	,,	110·03	0·950
0·002	112·07	,,	112·07	0·968
0·001	113·14	,,	113·14	0·977
0·0005	113·88	,,	113·88	—
0·0002	114·56	,,	114·56	—
0·0001	115·01	,,	115·01	—
0·0000	115·8 $= \Lambda_\infty$	,,	115·8	1·000

It will be observed that the viscosity of moderately concentrated solutions of NaCl and $AgNO_3$ is greater than that of water; the viscosity of KCl solution is less than that of water.

HYDROCHLORIC ACID.

Concentration in Equivalents per Liter.	Λ_v.	η_v/η_0.	$\Lambda_v\ \eta_v/\eta_0$.	$a = \frac{\Lambda_v}{\Lambda_\infty}\ \eta_v/\eta_0$.
0·1	351·4	unity	351·4	0·925
0·05	358·4	—	358·4	0·944
0·02	365·5	—	365·5	0·962
0·01	369·3	—	369·3	0·972
0·005	372·6	—	372·6	0·981
0·002	375·3	—	375·3	0·988
0·001	375·9	—	375·9	0·990
0·0005	377·0	—	377·0	—
0·0002	377·8	—	377·8	—
0·0001	378·1	—	378·1	—
0·0000	380·0 $= \Lambda_\infty$	—	380·0	1·000

POTASSIUM SULPHATE.

Concentration in Equivalents per Liter.	Λ_v.	η_v/η_0.	$\Lambda v\ \eta_v/\eta_0$.	a.
1·0	71·6	1·101	78·8	·592
0·5	78·4	1·049	82·2	·618
0·2	87·7	1·021	89·5	·673
0·1	94·9	1·0111	96·0	.722
0·05	101·9	1·006	102·5	·771
0·02	110·3	1·0033	110·7	·832
0·01	115·8	1·0014	116·0	·872
0·005	120·3	unity	120·3	·905
0·002	124·6	,,	124·6	·937
0·001	126·9	,,	126·9	·954
0·0005	128·5	,,	128·5	—
0·0002	130·0	,,	130·0	—
0·0001	130·7	,,	130·7	—
0·0000	133 $= \Lambda_\infty$	,,	133	1·000

Barium Chloride.

Concentration in Equivalents per Liter.	Λ_v.	η_v/η_0.	$\Lambda_v \, \eta_v/\eta_0$.	α.
1·0	70·14	1·107	77·6	·642
0·5	77·29	1·052	81·3	·672
0·2	85·18	1·021	87·0	·720
0·1	90·78	1·011	91·8	·759
0·05	96·04	1·005	96·5	·798
0·02	102·53	1·002	102·7	·850
0·01	106·67	1·001	106·8	·883
0·001	115·6	unity	115·6	·956
0·0005	117·01	,,	117·01	—
0·0000	120·9 = Λ_∞	,,	120·9	1·000

Copper Sulphate.

Concentration in Equivalents per Liter.	Λ_v.	η_v/η_0.	$\Lambda_v \, \eta_v/\eta_0$.	α.
1·0	25·77	1·371	35·3	·309
0·2	37·66	1·064	40·1	·351
0·1	43·85	1·032	45·3	·396
0·05	51·16	1·016	52·0	·455
0·02	62·40	1·008	62·9	·550
0·01	71·74	1·004	72·0	·629
0·005	80·98	1·002	81·1	·709
0·002	91·94	1·001	92·0	·804
0·001	98·56	unity	98·56	·862
0·0005	103·56	,,	103·56	—
0·0002	107·95	,,	107·95	—
0·0001	109·95	,,	109·95	—
0·0000	114·4 = Λ_∞	,,	114·4	1·000

It will be noticed that salts, acids, etc., containing monovalent atoms tend to give rise to the greatest dissociation into ions; divalent solutes, *i.e.* electrolytes containing a divalent radicle, dissociate less, and trivalent still less. It is convenient to remember that salts of monovalent ions, *e.g.* the alkali salts, when at a concentration of $\frac{N}{10}$, are dissociated to approximately 85 per cent., while divalent salts are not higher than 70 per cent. and may be much less (*e.g.* $CuSO_4$ $\frac{N}{10}$ solution dissociation is only about 40 per cent.). Trivalent salts exhibit about 50 per cent. dissociation or less in $\frac{N}{10}$ solution (Noyes' Rule).[1]

---

[1] Recent investigations by G. N. Lewis seem to point to smaller values of α than those quoted (*Journ. Amer. Chem. Soc.*, 34, 1631, 1912).

It will be seen, however, when we compare these with the dissociation of some typical weak electrolytes in the next table, that the two sets are not even of the same order of magnitude. The examples given are typical, but it must be remembered that there is no sharp dividing line between strong and weak electrolytes, there being quite a continuous series of substances from one group to the other.

B. *The Extent of Dissociation in the case of Weak Electrolytes* (those which conduct current badly).

A typical example is that of *Acetic Acid* in water. The following data were obtained by Kendall (*Trans. Chem. Soc.*, **101**, 1283, 1912) for this acid at 25° C. :—

Dilution v in Liters.	Λ.	α.	100 α. (Percentage Dissociation.)
13·57	6·086	0·01570	1·570
54·28	12·09	0·03118	3·118
108·56	16·98	0·04380	4·380
434·2	33·22	0·08568	8·568
868·4	46·13	0·1190	11·90
1737·0	63·60	0·1641	16·41
infinite dilution . . .	$\Lambda_\infty = 387{\cdot}7$	1·000	100·0

It will be observed that at a dilution $\frac{N}{1000}$ the fraction dissociated is only about 12 per cent., while in the case of HCl it is 100 per cent.

An interesting point is how the value 387·7 for Λ_∞ for acetic acid is arrived at. It is evident that throughout the range of the dilutions employed, even up to 1737, the Λ shows no sign of reaching a limiting value as it did in the case of the strong electrolytes mentioned. The true value for Λ when dissociation is complete cannot as a matter of fact be obtained directly for weak electrolytes, because at the dilution which would have to be employed—it would be several millions of liters—the observed conductivity would be practically identical with the value for the water, for even the best conductivity water contains, under ordinary conditions, slight traces of impurities, *e.g.* CO_2, which give to it a certain amount of conductivity quite sufficient to mask any effect due to the acetic acid were the solution so dilute as to allow of the acetic acid being completely dissociated. The method of determining Λ_∞ is based on Kohlrausch's Law of the independence of the mobility values of the ions. It is a remarkable fact that even although an acid—as acetic acid—may be extremely weak, its potassium or sodium salt is dissociated to practically the same extent in water as an inorganic salt like NaCl. We can therefore easily observe the equivalent conductivity of sodium acetate when the dissociation is complete, and knowing previously the mobility of the sodium ion we get by subtraction the mobility of the acetanion CH_3COO'. Now if we add to this the already known mobility of $H^{\cdot}$, we get as a result the Λ_∞ for acetic acid.

This is how the number 387·7 was obtained above. Since $H^{\cdot}$ itself contributes the value 347, it is evident that it has the predominating influence, so that practically all acids have approximately the same value for Λ_∞.

As a typical base which is a weak electrolyte one may instance ammonia. The following values hold for 25° C. :—

v.	Λ.	a.
8	3·20	0·0135
16	4·45	0·0188
32	6·28	0·0265
64	8·90	0·0376
128	12·63	0·0533
256	17·88	0·0754
	$\Lambda_\infty = 237$	

The base here considered is NH_4OH, which gives rise to $NH_4^{\cdot}$ and OH' ions to the extent indicated by a.

An $\frac{N}{10}$ solution of NH_3 is therefore about 1·5 per cent. dissociated, while NH_4Cl is 85 per cent. dissociated—a very striking example of the phenomenon alluded to above, *viz.* that the *salt* formed from a weak acid or weak base is itself a strong electrolyte. This is even true in the case of *ammonium acetate* where *both* acid *and* base are weak.

THE FUNDAMENTAL EQUILIBRIUM EQUATION FOR IONS. OSTWALD'S "DILUTION LAW".

Let us take a substance AB, which in solution partially dissociates into 2 ions, $A^{\cdot}$ (cation) and B' (anion), according to the equation—

$$AB = A^{\cdot} + B'.$$

Now, knowing that substances in solution behave in an analogous manner to gases, we apply the law of mass action, and find the equilibrium constant K given by—

$$\frac{[A^{\cdot}] \times [B']}{[AB]} = K$$

(Where square brackets denote concentration terms. The equilibrium is reached instantaneously.)

Since the reaction is a dissociation it is more usual to call K the dissociation constant. Further, the concentrations of cation and anion are equal, since the solution must be electrically neutral. If we consider the case in which one mole of the original solute has been dissolved in v liters, and has undergone dissociation to the extent a, *i.e.* there are $(1 - a)$ undissociated molecules and a cations and a anions, the mass action expression becomes—

$$\frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{\frac{1 - \alpha}{v}} = \frac{\alpha^2}{(1 - \alpha)v} = \mathrm{K}.$$

K should be independent of v (the dilution), but, of course, dependent upon temperature.

Now writing $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, the above expression may be put in the form—

$$\frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)v} = \mathrm{K}.$$

This equation in a slightly different form was first put forward by Ostwald in 1888 (*Zeitsch. physik. Chem.*, **2**, 36), who gave to it the name of the *dilution law.* It was investigated at greater length by Ostwald in a later paper (*ibid.*, **2**, 270, 1888) as regards its applicability to acids in aqueous solution. The following example, already given in part, is taken from Kendall's paper, *loc. cit.* :—

ACETIC ACID AT 25° C.

Volume of Solution v (liters) containing one gram-molecule of Solute.	Λ.	$\alpha \times 100$.	$\frac{\alpha^2}{(1-\alpha)v} = \mathrm{K}$.
13·57	6·086	1·570	0·00001845
27·14	8·591	2·216	1851
54·28	12·09	3·118	1849
108·56	16·98	4·380	1849
217·1	23·81	6·141	1851
434·2	33·22	8·568	1849
868·4	46·13	11·90	1850
1737·0	63·60	16·41	1854
3474·0	86·71	22·36	1855
6948·0	116·8	30·13	1870
∞	387·7	—	—
			Mean value of K = 0·0000185

To obtain measurements at such great dilution as 6948, *i.e.* one gram-molecule of acetic acid dissolved in 6948 liters, it is essential that the water employed as solvent shall be extremely pure. The specific conductivity of the water employed in the above measurements by Kendall was $0 \cdot 90 \times 10^{-6}$ reciprocal ohms.

The constancy of K is very good, the value being independent of v.

Reference may also be made to earlier papers upon the same subject (Ostwald, *Zeitsch. physik. Chem.*, **2**, 270; *ibid.*, **3**, 170, 241, 369, 1889; Bredig, *ibid.*, **13**, 289, 1894).

Ostwald succeeded in confirming the dilution law for 250 acids.

These were all weak acids. Similarly, Bredig found the law applicable in the case of 50 bases investigated by him.

By way of illustration, Bredig's results for ammonia and methylamine at 25° C. are given here :—

AMMONIA.

v liters.	Λ.	100 × α.	K.
8	3·20	1·35	$2·3 \times 10^{-5}$
16	4·45	1·88	2·3
32	6·28	2·65	2·3
64	8·90	3·76	2·3
128	12·63	5·33	2·3
256	17·88	7·54	2·4
	$\Lambda_\infty = 237$		
			Mean $2·3 \times 10^{-5}$

METHYLAMINE.

v liters.	Λ.	100 × α.	K.
8	14·1	6·27	$5·2 \times 10^{-4}$
16	19·6	8·71	5·2
32	27·0	12·0	5·1
64	36·7	16·3	5·0
128	49·5	22·0	4·9
256	65·4	29·1	4·7
	$\Lambda_\infty = 225$		
			Mean $5·0 \times 10^{-4}$

Bredig remarks that the probable source of the decrease in K in the last case is due to some CO_2, which, of course, affects the result the more the greater the dilution. It will be noted that the K for methylamine is twenty times greater than that for ammonia, *i.e.* methylamine is the stronger base. At similar dilutions the CH_3NH_2 (*i.e.* CH_3NH_3OH) is more dissociated than ammonia (*cf.* the α column). For these substances, which are only slightly dissociated, ***the ratio of the degrees of dissociation of the substances at the same dilution is given by the ratio of the square root of the dissociation constants.***

Thus
$$K_{NH_4OH} = \frac{\alpha^2}{(1 - \alpha)v},$$

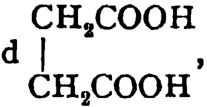
and since α is very small compared to unity, we may write—

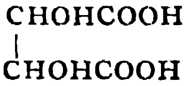
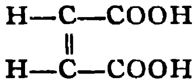
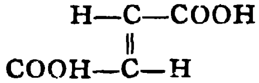
$$K_{NH_4OH} = \frac{\alpha^2}{v}.$$

Similarly, $$K_{CH_3NH_3OH} = \frac{\alpha_1^2}{v},$$

and hence, $$\frac{\alpha}{\alpha_1} = \sqrt{\frac{K_{NH_4OH}}{K_{CH_3NH_3OH}}}.$$

Besides the investigations of Ostwald and Bredig, a large number of other substances have been investigated (notably by Walker and his pupils), with the result that the dilution law, which is simply the law of mass action applied to the equilibrium of undissociated molecules and ions, has been verified in several hundred instances (see Lunden, *Ahrens Sammlung*, vol. 14).

An interesting phenomenon was noticed and explained by Ostwald in connection with the dissociation of the dibasic organic acids, *e.g.* malonic acid $CH_2(COOH)_2$, succinic acid  $\begin{array}{l}CH_2COOH\\ |\\ CH_2COOH\end{array}$, etc. These contain two carboxyl groups, and there is the possibility, therefore, of dissociation giving 2 $H^\cdot$ ions. It was found, however, that the ordinary dilution law, which only assumes a binary dissociation, X' and $H^\cdot$, holds good for these dibasic acids up to very considerable dilution. It follows, therefore, that both H atoms are not split off as ions with the same ease, but that after one has left the molecule the remaining one is retained until the dilution is great. Ostwald finds an explanation of this in the presence of the negative charge on the univalent anion which makes more difficult the addition of a second negative charge, owing to the electrostatic law that like charges repel one another. In the following table some examples are given of the dissociation of such acids, the final column containing the values of the degree of dissociation α, which are reached before the ordinary dilution law begins to break down, *i.e.* to no longer give a constant, thereby indicating the splitting off of the second $H^\cdot$ ion. The position of the (COOH) groups in the molecule is of great importance, for it is evident that the electrostatic action must be greater the nearer are the negatively charged carboxyl "rests" to one another, so that in those cases in which the carboxyl groups are close together the second-stage dissociation takes place only at very high dilutions. Thus, in the case of maleic acid the carboxyl groups are contiguous, and the dilution has to be carried to the region at which the first-stage dissociation is practically complete (about 93 per cent.) before the second-stage dissociation begins to manifest itself. Compare this with fumaric acid, in which the carboxyl groups are farther apart, and the second-stage dissociation begins to be noticeable when the first stage has reached 50 per cent. Of course, one must assume that the second stage does commence even at the higher concentrations, but is negligibly small.

Acid.	Dilution v in liters at which second-stage Dissociation manifests itself.	Degree of first-stage Dissociation reached at Dilution v.
Malonic— $CH_2(COOH)_2$	256	0·46-0·58
Tartaric— $\begin{array}{l}CHOHCOOH\\ \mid\\ CHOHCOOH\end{array}$	128	0·30-0·40
Maleic— $\begin{array}{l}H—C—COOH\\ \quad\ \Vert\\ H—C—COOH\end{array}$	>1024	>0·93
Fumaric— $\begin{array}{r}H—C—COOH\\ \Vert\quad\quad\ \ \\ COOH—C—H\end{array}$	256	0·40-0·50

It will be observed that on the average the first-stage dissociation proceeds to the extent of 50 per cent. before the second-stage dissociation becomes apparent.

"THE ANOMALY OF STRONG ELECTROLYTES."

The electrolytes referred to in the previous section are all weak electrolytes. The most remarkable phenomenon in the equilibria relations of electrolytes in aqueous solution is that all (or nearly all) strong electrolytes—throughout the range of dilution 10-1000 liters—do not even approximately obey the dilution law. A few appear to do so, at least over a certain range of dilution, notably, amongst acids, dichloracetic acid, cyanacetic acid, and maleic acid, but these instances are relatively few in number.[1] All the ordinary inorganic salts (with the exception of cadmium and mercury (*ic*) halides, mercuric cyanide, and one or two ferric salts), all the ordinary inorganic acids and bases (with the exception of weak acids, such as H_2S, H_3BO_3, CO_2, HNO_2, SO_2, phosphorous acids, and NH_3) dissociate in such a manner that when one calculates the "constant" for each dilution,[2] it is found that the resulting numbers scarcely remain even of the same order of magnitude.

Thus taking the case of NH_4Cl at 18° C., which we have already cited, a calculation of the "constant" gives the following values for "K":—

---

[1] For further instances of acids see Abegg's *Electrolytic Dissociation Theory.*

[2] "α" being calculated from conductivity data.

NH_4Cl.

v.	Λ.	α.	Ostwald, "K."
1	90·7	0·750	2·2
2	94·8	0·784	1·4
10	103·5	0·856	0·51
20	107·8	0·892	0·37
100	114·2	0·945	0·16
500	118·0	0·976	0·08
1,000	119 0	0·985	0·065
5,000	120·4 } Λ_∞	1·000	—
10,000	120·9	,,	—
50,000	120·9	,,	—

The "constant" increases rapidly as the concentration increases. If, therefore, we assume that the law is obeyed at very great dilution (*i.e.* when $v = 1000$), we could conclude that some effect comes in which causes the dissociation to be too great at the greater concentrations. This may not be the case, however. The values for "α" were obtained by the conductivity method $\alpha = \frac{\Lambda_\infty}{\Lambda_\infty}$. The problem therefore resolves itself into this—is the law of mass action in error (*i.e.* not wide enough in its scope in its present simple form), or does the ratio of the equivalent conductivity at v to Λ_∞ not give a *true* measure of the dissociation? This point has not yet been settled.[1]

In general the values of α obtained from cryoscopic (freezing point) or ebullioscopic (boiling point) measurements agree fairly closely with those obtained from conductivity measurements, where such comparison is possible. It should be remembered, however, that the degree of accuracy reached by the freezing or boiling point method is much less than it is in the case of conductivity measurements.

On the other hand, there is nothing in the derivation of the dilution law which would lead us to suppose that it would hold only for the limiting case of very small dissociations, *e.g.* weak electrolytes. One would have expected it to hold for strong electrolytes as well. Abegg, in his *Electrolytic Dissociation Theory* (p. 126), favours the view that the dilution law, *i.e.* the law of mass action, is in essence correct, and a constant would be obtained in the case of strong electrolytes as well as for weak, if we possessed the true values of the dissociation. He considers that the discrepancies are due to secondary efforts entering in, such as complex formation among the ions themselves (which is known to exist, for example, in the case of cadmium salts), or, on the other hand, to the formation of ion hydrates, *i.e.* combination of the solvent with the ions.

For a critical review of the question the reader should consult a paper by Noyes (*St. Louis Congress Report*, 1904), which also appeared in *Science*, **20**, 577, 1904.

---

[1] This question is taken up again in Vol. II., Chap. VIII.

One point still remains to be mentioned in connection with the conductivity method of determining the dissociation. Drücker (*Zeitsch. physik. Chem.*, **49**, 563, 1904) was the first to emphasise that the principle may be correct, but the results in error because of error in the value for Λ_∞, and he also showed that a relatively small change in this value has very marked effect. He illustrated this with dichloracetic and trichloracetic acids. Jahn took up the same point (*Zeitsch. physik. Chem.*, **50**, 129, 1904), illustrating it by the alkali salts.[1] Thus, taking Kohlrausch's value for the Λ_∞ for KCl, *viz.* 129·07, and using this to calculate α and "K," the following results are obtained:—

KCl.

Concentration (C) grammoles per liter.	α.	Actual Concentration the Ions = C × α.	"K."
0·1	0·8680	0·08680	0·571
0·05	0·8968	0·04484	0·390
0·02	0·9295	0·01859	0·245
0·01	0·9486	0·009486	0·175
0·005	0·9638	0·004819	0·128
0·002	0·9785	0·001957	0·0895
0·001	0·9866	0·0009866	0·0726

It is only necessary, however, to alter the value of Λ_∞ from 129·07 to 127·65 (a quite empirical change, of course) to bring at least the *most dilute* solutions into approximate accord with the dilution law; thus—

C.	α.	C × α.	K.
0·01	0·9591	0·009591	0·225
0·005	0·9746	0·004873	0·187
0·002	0·9895	0·001979	0·187

The same conclusion holds for other strongly dissociated salts. Jahn corroborated this conclusion, using the freezing-point method with great care and accuracy. His results were published (*Zeitsch. physik. Chem.*, **59**, 31, 1907) after his death in a paper edited by Nernst. It thus appears that *Ostwald's Dilution Law holds in the limiting cases both when the dissociation is very small and when it is extremely great.* For intermediate values it appears to break down though its failure may after all not be inherent in itself. In this connection the reader should consult a recent paper by Washburn and his collaborators (*J. Amer. Chem. Soc.*, Jan., 1918) in which it is shown that Drücker's method is incorrect. At the same time it is shown that a strong electrolyte such as KCl does actually obey the law of mass action at dilutions greater than 10,000.

---

[1] See also Flugel, *Zeitsch. physik. Chem.*, **79**, 586, 1912.

Although Ostwald's Dilution Law does not hold in general for strong electrolytes throughout the ordinary range of dilution ($v = 10$ to $v = 1000$), two other dilution laws have been found to give a constant for binary electrolytes. These, however, differ essentially from that of Ostwald, in that they are absolutely empirical, *i.e.* they are not deduced from the law of mass action. One is due to Rudolphi—and hence called Rudolphi's Dilution Formula (*Zeitsch. physik. Chem.*, **17**, 385, 1895). It has the form—

$$\frac{\alpha^2}{(1 - \alpha)\sqrt{v}} = \text{constant.}$$

It thus differs from Ostwald's expression in having $\sqrt{v}$ substituted arbitrarily for v. The constancy of the K is illustrated for the case of ammonium chloride at 18° C.—

v.	$\frac{\alpha^2}{(1 - \alpha)\sqrt{v}}$
10	1·55
20	1·56
100	1·47
500	1·46
1000	1·47
1667	1·60
5000	1·53
	Mean 1·51

A second empirical formula is due to van 't Hoff (*Zeitsch. physik. Chem.*, **18**, 301, 1895). It may be written—

$$\frac{\alpha^{\frac{3}{2}}}{(1 - \alpha)\sqrt{v}} = \text{constant}$$

or

$$\frac{\alpha^3}{(1 - \alpha)^2 v} = \text{constant.}$$

that is—

$$\frac{(\text{concentration of \textit{either} of the ions})^3}{(\text{concentration of undissociated substance})^2} = \text{constant.}$$

It will be observed that Ostwald's Dilution Law states—

$$\frac{(\text{concentration of either of the ions})^2}{(\text{concentration of undissociated substance})} = \text{constant.}$$

The following table indicates the values of the van 't Hoff constant for a few strong electrolytes at 18° C.

v.	KNO_3.	$MgSO_4$.	HCl.	KCl.	NaCl.	KBr.
2	1·63	—	4·41	2·49	1·87	2·44
4	1·67	0·162	4·87	2·23	1·71	2·55
8	1·68	0·156	4·43	2·1	1·6	2·28
16	1·72	0·151	4·72	1·94	1·4	2·38
32	1·82	0·151	5·29	1·87	1·43	2·41
64	1·88	0·158	—	1·72	1·38	2·72

An attempt to give an approximate "physical" significance to van 't Hoff's formula was made by Kohlrausch (*Zeitsch. physik. Chem.*, **18**, 662, 1895). Denoting by C_i the concentration of each of the ions, by C_s the concentration of the undissociated substance, van 't Hoff's formula may be written $\frac{C_i^3}{C_s^2}$ = constant, and therefore $\frac{C_i}{C_s^{\frac{2}{3}}}$ = constant = k_2, say. This may also be put in the form—

$$\frac{C_i}{C_s} = \frac{k_2}{C_s^{\frac{1}{3}}}.$$

Now $C_s^{\frac{1}{3}}$ is the "linear density" of the undissociated molecules, or $C_s^{-\frac{1}{3}}$ is the mean distance apart of the undissociated molecules. Calling this distance r, the above expression may be written—

$$\frac{C_i}{C_s} = k_2 r_s$$

$$\text{or } \frac{\text{concentration of either ion}}{\text{concentration of undissociated substance}} = \left\{\begin{array}{l}\text{constant} \times \text{the} \\ \text{distance of} \\ \text{the molecules} \\ \text{apart.}\end{array}\right.$$

It must be borne in mind that there is no theoretical reason why either the Rudolphi or the van 't Hoff expression should yield a constant at all. Other expressions, also empirical or semi-empirical, have been proposed from time to time. Attention may be drawn to two of these which have a certain amount of theoretical basis, first, that proposed by Partington (*Trans. Chem. Soc.*, **97**, 1158, 1910), *viz.*—

$$\frac{\alpha^2}{(1 - \alpha)(v + p\alpha)} = K$$

where α denotes the degree of dissociation at the dilution v, and p is a constant which has to be determined by experiment; and, secondly,[1] the expression proposed by Kendall (*Trans. Chem. Soc.*, **101**, 1283, 1912), *viz.*—

$$\frac{\alpha^2}{(1 - \alpha)v} = k + c\frac{1 - \alpha}{\alpha}$$

where c is a constant which has also to be determined by experiment.

---

[1] Partington has shown that Kendall's formula is a particular case of his own expression (*Proc. Chem. Soc.*, 1914).

Partington's expression holds only very approximately for strong electrolytes, the constant passing through a maximum. Further, Partington's expression reduces to that of Ostwald in the limit when a is small compared to unity. It leaves the question still open, however, whether the law of mass action in principle is applicable to electrolytic dissociation when the latter is large.

Isohydric Solutions.

When we mix two electrolytic solutions together, we cannot in general calculate the conductivity of the mixed solutions from those of the components by the simple mixture law, since each dissolved substance affects the dissociation of the other, and thus alters the total number of ions present. There must be, however, certain solutions for which the mixture law does hold, *i.e.* the dissociation of each solution is not altered on mixing. These are called isohydric solutions. The experimental method of testing for isohydry is by determining the conductivity (a or b) of each solution separately, and likewise that of the resultant mixture (A). Isohydry obtains if the mixture law holds good, *i.e.* if the observed value—

$$A = a\frac{v_a}{v_a + v_b} + b\frac{v_b}{v_a + v_b}$$

where v_a and v_b are the volumes of each separate solution, and the dilution is sufficiently great to warrant writing the final mixture volume as simply $v_a + v_b$. A solution of, say, $\frac{N}{10}$ concentration would comply with such a condition, and at the same time the degree of dissociation would not necessarily be complete—for weak electrolytes, the dissociation at this concentration would be very small indeed; for strong electrolytes, it might be about 80 per cent.

Now what is the theoretical condition for isohydry—that is, what is the condition that on mixing two solutions no change in the dissociation of each may arise—a state of things which is shown to exist by the mixture law holding for the conductivity?

Let us take two solutions, one containing one mole of the acid HA, the other containing one mole of the acid HA_1. Let the volume of the first be v_a and that of the second be v_b. Suppose the degrees of dissociation are respectively a_a and a_b. If both acids are weak, they obey Ostwald's dilution law. That is to say, for HA we have—

$$\frac{a_a^2}{(1 - a_a)v_a} = k_a \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for HA_1 we have—

$$\frac{a_b^2}{(1 - a_b)v_b} = k_b \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now let us assume that these solutions are actually isohydric, that is to say, that on mixing them it is found that the mixture law holds for the observed specific conductivity when this is expressed in terms of the separate conductivities of each, assuming that their respective degrees of dissociation are the same before and after mixing. Since the solutions are supposed to be fairly dilute, there will be no contraction or other chemical effect coming in, and the total final volume is $v_a + v_b$.

Under these conditions the mass of hydrogen ion is $a_a + a_b$, and applying the dilution law to the case of the acid HA in the mixture, we get—

$$\frac{(a_a + a_b)a_a}{(1 - a_a)(v_a + v_b)} = k_a \quad . \quad . \quad . \quad . \quad (3)$$

Dividing (3) by (1), we get—

$$\frac{(a_a + a_b)v_a}{(v_a + v_b)a_a} = 1$$

or

$$\frac{a_a + a_b}{a_a} = \frac{v_a + v_b}{v_a}$$

whence

$$\frac{a_b}{a_a} = \frac{v_b}{v_a}$$

or

$$\frac{a_b}{v_b} = \frac{a_a}{v_a}.$$

But $\frac{a_b}{v_b} = \left\{\text{concentration of H}^{\cdot}\text{ ion in the solution of the acid HA}_1\text{ by itself,}\right.$

likewise $\frac{a_a}{v_a} = \left\{\text{concentration of H}^{\cdot}\text{ ion in the solution of the acid HA by itself.}\right.$

Therefore, we find that when solutions are isohydric they each contain the common ion—in this case the hydrogen ion—at the same concentration. We may apply this conclusion of the electrolytic dissociation theory in the reverse sense, *i.e.* if we make two solutions containing a common ion so that the common ion has the same concentration value in both, then the dissociation of each of these solutions will be unaltered upon mixing them together in *any proportions.*

We thus are dealing with what at first sight is rather a remarkable phenomenon, *viz.* that although the volume of the system—say the HA_1 solution—is increased by addition of HA_2 solution, the dissociation of each of these acids is unchanged. Here we have apparently an instance of degree of dissociation being independent of dilution. It must be remembered, however, that there is in reality no disagreement with the principle of dissociation progressing with dilution, for by dilution in the ordinary sense is meant increase in volume due to addition of pure solvent alone. Further, it does not matter what amount of the second solution we may add, provided the solutions are isohydric. The first investigation upon isohydry and the demonstration that such exists is that of Arrhenius (*Wiedemann's Annalen,* **30**, 54, 1887). His work was extended in a later paper (*Zeitsch. physik. Chem.*, **2**, 284, 1888), from which the following table is taken. A number of solutions of different acids were prepared of such concentrations that the specific conductivity of any mixture of two was given quantitatively by the mixture law. Arrhenius then calculated from the conductivity of each separate solution what the degree of dissociation was, and thence the hydrogen ion concentration in each case. The values for the hydrogen ion concentration of each of the single acids at various dilutions (these dilutions being such that the mixture law applied to them when mixed) are given in the horizontal columns, and it will be seen that the solutions contain almost the same amount of hydrogen ion. In the table the concentration terms are milligrams per liter.

HCl.	$(COOH)_2$.	$C_4H_6O_6$ Tartaric.	HCOOH.	CH_3COOH.	Mean Value for [H·].
151·5	152·6	—	—	—	152·1
42·3	35·1	—	—	—	38·7
22·03	21·37	19·07	—	—	20·82
4·48	4·09	4·17	4·42	3·96	4·18
1·33	1·24	1·25	1·44	1·33	1·32
0·379	0·397	0·381	—	0·402	0·390

Again, it will be remembered in deducing the equivalence of the concentration of the common ion in the case of isohydric solutions as a consequence of the electrolytic dissociation theory, we only made use of general volume terms v_a and v_b. The formation of isohydric solutions, therefore, should not depend upon the addition of any particular volume of the second solution to the first. That is to say, the mixture law should be obeyed for any case when once it has been shown to hold for the special case, *viz.*, a mixture formed of equal volumes ($v_a = v_b$). Arrhenius (*l.c.*, 1887) has verified this in a number of instances. He found, for example, that a solution of H_3PO_4, specific conductivity (in reciprocal mercury resistance units) $223·7 \times 10^{-8}$, is isohydric with a solution of HCl, specific conductivity $167·4 \times 10^{-8}$ (by the method of trial and error, using equal volumes of each acid, so that the specific conductivity, as calculated by the mixture law, took the simple shape $A = \frac{a + b}{2}$). He now mixed these in *different* volume proportions, with the following result :—

	Specific Conductivity.	
	Observed.	Calculated.
7·5 c.c. H_3PO_4 solution + 2·5 c.c. HCl solution	$209·5 \times 10^{-8}$	$209·9 \times 10^{-8}$
5·0 c.c. ,, ,, + 5·0 c.c. ,, ,,	$195·1 \times 10^{-8}$	$195·6 \times 10^{-8}$
2·5 c.c. ,, ,, + 7·5 c.c. ,, ,,	$181·7 \times 10^{-8}$	$181·2 \times 10^{-8}$

The calculated conductivity is the result given by the mixture law expression—

$$\left[a\frac{v_a}{v_a + v_b} + b\frac{v_b}{v_a + v_b}\right].$$

The agreement between the last two columns bears out the theoretical conclusion. Even closer agreement was obtained in the case of mixtures of oxalic acid and acetic acid, as likewise for mixtures of acetic acid and hydrochloric acid. A few of the data obtained in the latter case are given here.

It was found (by mixing equal volumes and altering the concentration of the acids singly) that a solution of acetic acid, specific conductivity $12·18 \times 10^{-8}$, was isohydric with a solution of HCl, specific conductivity $14·54 \times 10^{-8}$. These solutions were then mixed in different volume proportions, as follows:—

	Specific Conductivity.	
	Observed.	Calculated.
10 c.c. CH_3COOH solution + 1 c.c. HCl solution	$12·37 \times 10^{-8}$	$12·39 \times 10^{-8}$
10 c.c. " " + 4 c.c. " "	$12·87 \times 10^{-8}$	$12·85 \times 10^{-8}$
10 c.c. " " + 7 c.c. " "	$13·18 \times 10^{-8}$	$13·15 \times 10^{-8}$
10 c.c. " " + 15 c.c. " "	$13·58 \times 10^{-8}$	$13·59 \times 10^{-8}$
5 c.c. " " + 10 c.c. " "	$13·81 \times 10^{-8}$	$13·76 \times 10^{-8}$
1 c.c. " " + 10 c.c. " "	$14·34 \times 10^{-8}$	$14·33 \times 10^{-8}$

It is rather remarkable that the above independence of volume, which was theoretically predicted on the basis of the dilution law (*i.e.* the law of mass action) which holds for weak electrolytes alone, should have been also verified for mixtures containing strong acids such as hydrochloric.

We may now draw attention to a result which is indeed almost self-evident, namely, that solutions which are isohydric with one and the same solution are isohydric with one another. Arrhenius verified this in the case of a number of acids.

While it is in general possible to prepare isohydric solutions—the criterion for isohydry being that the conductivity in the case of the resulting mixture obeys the mixture law—it is occasionally found impossible to do so. Thus let us take a solution of HCl $\frac{N}{42}$ (Arrhenius, *l.c.*, 1887), and we require to find the corresponding isohydric acetic acid solution. Arrhenius had previously found that 1N acetic was isohydric with $\frac{1}{120}$N HCl. The acetic sought for in the present case must be still stronger than 1N. Experimentally the following differences were found between the observed conductivity A for the mixture and the value calculated by the mixture law:—

1N	acetic gave a difference		– 19·0
2·5	”	”	– 24·4
5	”	”	– 33·3
10	”	”	– 50·0

On increasing the acetic acid content, therefore, instead of reaching a point where the above difference will vanish, we find this difference steadily increasing. The conductivity of acetic acid goes through a maximum and then falls instead of increasing continuously with the concentration. This effect is due to the increased friction owing to the large number of undissociated molecules which are present along with the ions at the higher concentration. It is found impossible to reach a high enough value for the specific conductivity in the case of the acetic acid solution such that the value given by the mixture law when the mixture is made approximates to the observed conductivity. Even the maximum value of the acetic acid is too low. The remarkable fact, however, is that we must suppose it quite possible that solutions of CH_3COOH of the same $H^{\cdot}$ ion concentration as $\frac{N}{42}$ HCl can be prepared, and that, therefore, isohydric solutions can be obtained if we look upon equality of the $H^{\cdot}$ ion as the criterion of isohydry. The apparent anomaly is due to the fact that the conductivity of concentrated CH_3COOH solutions is not the correct measure of the $H^{\cdot}$ ion concentration, *i.e.* we cannot write $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$, since the mobilities are no longer the same at the dilution v as they are at infinite dilution.

We now pass on to the application of the principle of isohydry to solutions which consist of mixtures of several substances in equilibrium. We introduce the idea of an imaginary septum or imaginary septa by which we can suppose the mixture divided up into isohydric solutions of the constituent electrolytes. Thus, if we take a dilute mixture of NaCl and KCl, these substances are dissociated practically to the same degree at the same dilution, so that we might imagine the septum dividing the solution into two equal parts, one part containing only KCl, the other only NaCl, the solutions being isohydric. In the case of the mixture of a solution of sodium acetate (which is largely dissociated), and acetic acid (which is only slightly dissociated), the septum would no longer be placed so as to divide the whole solution in half in order to get the acetanion CH_3COO' concentration equal on both sides, but would lie far over towards the acetic acid side.

It is evident that we can regard any mixture of the two acids as composed of such quantities of each pure acid solution as are isohydric with one another. This case may be treated in the following way[1]:—

In the mixture suppose c_1 to be the total concentration of the acid HA_1, c_2 that of HA_2, $[H^{\cdot}]$ the total concentration of $H^{\cdot}$ ions (determined, say, by their catalytic effect upon the inversion of cane sugar), and finally α_1 and α_2 the degrees of dissociation of the acids (which are supposed to obey the dilution law). We have then the following relations:—

---

[1] In this discussion I have followed closely the treatment given by Abegg, *Electrolytic Dissociation Theory*, p. 63 *seq.*

$$k_1 = \frac{[H^\cdot][A'_1]}{[HA_1]} = \frac{[H^\cdot]\alpha_1 c_1}{(1 - \alpha_1)c_1} = [H^\cdot]\frac{\alpha_1}{1 - \alpha_1}.$$

Similarly,

$$k_2 = \frac{[H^\cdot][A'_2]}{[HA_2]} = [H^\cdot]\frac{\alpha_2 c_2}{(1 - \alpha_2)c_2} = \frac{[H^\cdot]\alpha_2}{1 - \alpha_2},$$

from which we obtain—

$$\frac{1}{\alpha_1} = 1 + \frac{[H^\cdot]}{k_1}; \quad \frac{1}{\alpha_2} = 1 + \frac{[H^\cdot]}{k_2}.$$

The sought-for concentrations x_1 and x_2 of the pure solutions, whose degrees of dissociation are also α_1 and α_2, are given by the relations—

$$k_1 = \frac{\alpha_1^2 x_1}{1 - \alpha_1} \text{ or } x_1 = k_1\frac{1 - \alpha_1}{\alpha_1^2}$$

$$k_2 = \frac{\alpha_2^2 x_2}{1 - \alpha_2} \text{ or } x_2 = k_2\frac{1 - \alpha_2}{\alpha_2^2}.$$

On substituting in these two equations the values for k_1 and k_2 found above, we obtain—

$$x_1 = [H^\cdot]\frac{\alpha_1}{1 - \alpha_1} \cdot \frac{1 - \alpha_1}{\alpha_1^2} = [H^\cdot]\frac{1}{\alpha_1}$$

and

$$x_2 = [H^\cdot]\frac{1}{\alpha_2},$$

or, on substituting k_1 and k_2 respectively—

$$x_1 = [H^\cdot]\left\{1 + \frac{[H^\cdot]}{k_1}\right\} = [H^\cdot] + \frac{[H^\cdot]^2}{k_1}$$

$$x_2 = [H^\cdot]\left\{1 + \frac{[H^\cdot]}{k_2}\right\} = [H^\cdot] + \frac{[H^\cdot]^2}{k_2}$$

in place of which, for small k values, the approximation usually suffices—

$$x_1 = \frac{[H^\cdot]^2}{k_1} \text{ and } x_2 = \frac{[H^\cdot]^2}{k_2}$$

or

$$\frac{x_1}{x_2} = \frac{k_2}{k_1}.$$

That is, two acids upon being mixed will not affect each other's dissociation provided their separate concentrations are such as to be inversely proportional to their dissociation constants.

CONSIDERATION OF THE CASE IN WHICH THE ACIDS DO AFFECT THEIR MUTUAL DEGREE OF DISSOCIATION.

The effect of addition of an acid to the solution of another.—Let us denote the first acid by HA_1 and the second by HA_2. Let the corresponding dissociation constants be k_1 and k_2 (measured for each acid separately).

Let c_1 and c_2 be the total concentration of each acid in the mixture, and when in the mixed state let the degrees of dissociation be respectively a_1 and a_2.

In the mixture—

$$\begin{aligned} \text{The concentration of the } H^{\cdot} \text{ ions} &= a_1c_1 + a_2c_2 \\ \text{,,} \quad \text{,,} \quad A_1 \text{ ,,} &= a_1c_1 \\ \text{,,} \quad \text{,,} \quad A_2 \text{ ,,} &= a_2c_2 \end{aligned}$$

and therefore we have, applying Ostwald's Dilution Law—

$$\begin{aligned} k_1(1 - a_1)c_1 &= a_1c_1(a_1c_1 + a_2c_2) \\ k_2(1 - a_2)c_2 &= a_2c_2(a_1c_1 + a_2c_2). \end{aligned}$$

Now if the acids are both weak and at moderate dilutions, a_1 and a_2 may be neglected compared to $(1 - a_1)$ and $(1 - a_2)$, *i.e.* $(1 - a_1) = (1 - a_2)$ approximately. Hence in this case—

$$\frac{k_1}{k_2} = \frac{a_1}{a_2}.$$

That is to say, the actual degree of dissociation which each possesses when mixed is proportional to the respective dissociation constant.

Hence the acid with the larger dissociation constant will be dissociated to the larger extent in the mixture. The most interesting case is, however, when we add a strong acid—say, HCl—to a solution of a weak acid—say, acetic—and investigate what happens. Calling k_1 the dissociation constant of acetic acid, then with the same notation as before we obtain—

$$k_1 = \frac{a_1}{1 - a_1}(a_1c_1 + a_2c_2).$$

Further, we can write, as before, $(1 - a_1) = 1$, with even greater exactness, for now, owing to the addition of the strong acid, we have added a large quantity of $H^{\cdot}$ ions, and therefore have thrown back the dissociation of the weak acid. This must necessarily happen if the weak acid obeys the dilution law, for the product of the concentrations of the two ions divided by the concentration of the undissociated molecules, must be constant under all circumstances. For the sake of simplicity, let us assume in the above case that the dissociation of the HCl is complete, *i.e.* $a_2 = 1$. Then we have—

$$k_1 = a_1(a_1c_1 + c_2) = a_1^2c_1 + a_1c_2.$$

Now a_1 (the degree of dissociation of the weak acid) is a small number, much less than unity. The higher power may, therefore, be neglected compared with terms containing the first power, that is—

$$k_1 = a_1c_2$$

or

$$a_1 = \frac{k_1}{c_2}.$$

In words, the degree of dissociation (a_1) of the weak acid in the mixture is directly proportional to its dissociation constant, and inversely as the concentration of the strong acid. By adding a large quantity of HCl. therefore, to acetic acid solution, we can cause the acetic acid dissociation practically to vanish, *i.e.* there is practically no acetanion in the solution. The same behaviour is noticed in the case of bases, and, further, instead of adding strong acids (or strong bases), we may also add salts which are likewise strongly dissociated. Thus, in analytical chemistry, the case occurs in which we add NH_4Cl to NH_3 solution before employing it to precipitate certain hydroxides. The effect of the NH_4Cl is to drive back the dissociation of the NH_4OH so that extremely little OH′ ion exists in solution. Owing to the very slight solubility of the hydroxides of metals such as Fe, Al, Zn, even the small quantity of OH′ thus left is sufficient to yield hydroxide in excess of the solubility, but the OH′ ion is not sufficient to form $Mg(OH)_2$ in quantities sufficiently great to exceed its much greater solubility, and hence this base is not precipitated, separation of magnesium being thereby effected.[1] This problem belongs, however, to heterogeneous equilibrium and will be dealt with later.

As an illustration of the phenomenon of throwing back the dissociation one may give a few measurements made by Arrhenius (1889) of the velocity of inversion of cane sugar by means of the H˙ ion of acetic acid, when varying quantities of sodium acetate are added (which, being a salt, is largely dissociated, and hence gives rise to large quantities of acetanion CH_3COO', and this, in accordance with the principle of mass action, causes the H˙ ion from the acid to be diminished).

0·25 N ACETIC ACID + C NORMAL SODIUM ACETATE.

	C = 0.	0·0125.	0·025.	0·05.	0·125.	0·25.
Velocity of reaction—observed	$0{\cdot}75 \times 10^3$	$0{\cdot}122 \times 10^3$	$0{\cdot}070 \times 10^3$	$0{\cdot}040 \times 10^3$	$0{\cdot}019 \times 10^3$	$0{\cdot}0105 \times 10^3$
Velocity of reaction—calculated[2]	$0{\cdot}74 \times 10^3$	$0{\cdot}129 \times 10^3$	$0{\cdot}070 \times 10^3$	$0{\cdot}038 \times 10^3$	$0{\cdot}017 \times 10^3$	$0{\cdot}0100 \times 10^3$

---

[1] There is a certain amount of complication here as apparently a complex ammonium magnesium chloride is formed at the same time.

[2] This initial calculated value of the velocity constant is obtained as a result of other experiments on the catalytic effect of H˙ ion, which show that with moderate approximation the velocity of catalysis is directly proportional to the H˙ ion. At the date of Arrhenius' measurements the catalytic effect of the undissociated molecule of acid was scarcely considered sufficiently. In the case of acetic acid, however, the effect of the molecule is small.

THEORY OF THE DISTRIBUTION OF A BASE AMONG TWO OR MORE ACIDS.

Let us consider the distribution which takes place when a ***strong*** base BOH is added to a mixture of two ***weak*** acids, HA_1 and HA_2, the quantity of base being insufficient to neutralise both acids completely. In 1 liter of solution suppose there are—

b moles of BOH
c_1 " HA_1
c_2 " HA_2
$c_1 + c_2 > b$

NOTE.—These terms do not represent *actual* concentration values, since reaction proceeds immediately the base is added. They only serve, therefore, to express the composition which the mixture would have if no reaction took place.

Suppose, further, that a fraction x of each mole of the base reacts with the acid HA_1, then $(1 - x)$ is the fraction of one mole of base which is left for the acid HA_2. In the mixture we have, therefore, assuming complete dissociation of the salt:—

bx gram-molecules of salt BA_1 or bx moles of A'_1
$b(1 - x)$ " " BA_2 or $b(1 - x)$ " A'_2
also $(c_1 - bx)$ moles of nearly undissociated acid HA_1
$c_2 - b(1 - x)$ " " " HA_2

If k_1 and k_2 are the respective dissociation constants of the acids, we have—

$$k_1 = \frac{[H^{\cdot}][A'_1]}{[HA_1]} = \frac{[H^{\cdot}]bx}{c_1 - bx}$$

$$k_2 = \frac{[H^{\cdot}][A'_2]}{[HA_2]} = \frac{[H^{\cdot}][b(1 - x)]}{[c_2 - b(1 - x)]}$$

so that

$$\frac{k_1}{k_2} = \frac{x}{1 - x} \cdot \frac{c_2 - b(1 - x)}{c_1 - bx}$$

or in words:—

$$\frac{x}{1 - x} = \frac{\text{concentration of salt } BA_1}{\text{concentration of salt } BA_2} = \frac{k_1 \times \text{concentration of acid } HA_1}{k_2 \times \text{concentration of acid } HA_2}$$

The distribution ratio $\frac{x}{1 - x}$ is thus a function of the dissociation constants of the competing acids.

The value of x is given by the following equation—

$$x = \frac{\left(\frac{k_1}{k_2} - 1\right)b + \frac{k_1}{k_2}c_1 + c_2 \pm\sqrt{\left[\left(\frac{k_1}{k_2} - 1\right)b + \frac{k_1}{k_2}c_1 + c_2\right]^2 - 4\left[\frac{k_1}{k_2} - 1\right]\frac{k_1}{k_2}bc_1}}{2\left(\frac{k_1}{k_2} - 1\right)b.}$$

The above relations can be simplified in certain cases. Thus, when we add one equivalent of the base to a mixture containing one equivalent of each acid, then $b = c_1 = c_2$, and—

$$\frac{k_1}{k_2} = \frac{x}{1 - x} \cdot \frac{bx}{b(1 - x)} = \frac{x^2}{(1 - x)^2}$$

or

$$\frac{x}{1 - x} = \sqrt{\frac{k_1}{k_2}}$$

To determine the distribution ratio, therefore, we have to determine the dissociation constant of each acid—if such a constant exists. The most usual method of determining k_1 or k_2 is by means of the electrical conductivity. Catalytic methods of estimating $H^\cdot$ ion concentrations may also be employed.

In the case of *strong* acids which possess no dissociation constant, the preceding formula is inapplicable. In this case the most direct method is to actually carry out a distribution experiment according to the method of Thomsen (thermo-chemical method) or that of Ostwald (volume method). We may briefly consider these.

In order to compare the strengths of two acids, the comparison must be made under the same conditions, the essential condition being secured when the reacting system is a single homogeneous phase, *e.g.* a solution. Thus it is known that HCl is a stronger acid than H_2SO_4, yet by evaporating almost to dryness a solution of a chloride with H_2SO_4 present, it will be found that practically all the HCl has been expelled and replaced by H_2SO_4 in the salt, *i.e.* a sulphate is formed. The HCl is expelled, however, not because it is a weaker acid than H_2SO_4, but because it is more volatile, and escapes during the heating process. To compare the strengths or "avidities" of two acids, we have to measure the distribution of a base between them, the base being insufficient for complete neutralisation of both.

The Thermochemical Method of Thomsen.—When one equivalent of H_2SO_4 is neutralised by caustic soda in dilute solution, there is heat evolved, say *a* cals. When one equivalent of HCl is neutralised by the same amount of NaOH, there is a quantity of heat, say *b* cals., evolved (*b* is not very different from *a*, being a little smaller than *a*). Now take a solution containing one equivalent of Na_2SO_4, and add one equivalent of HCl. Thomsen noted a small heat absorption of *c* calories. If there had been no chemical action at all, there would have been no heat evolved or absorbed. If the HCl had completely expelled the SO_4 and formed NaCl, there would have been a heat absorption of $(a - b)$ cals. Thus, we might think of the process occurring in two stages—first a de-neutralisation or liberation of *all* the H_2SO_4, which would be accompanied by a heat *absorption* of *a* cals., and, secondly, a neutralisation of the HCl, which would be accompanied by an *evolution* of *b* cals., the process yielding a nett heat effect of $(a - b)$ cals. But a smaller heat absorption was noted, *viz.* *c* cals., where in this case *c* was about $\frac{11}{18}$ of $(a - b)$. If we assume that the amount of action is proportional to the heat effect, then the quantity of Na_2SO_4 which was transformed into NaCl was $\frac{c}{a - b}$, or about $\frac{11}{13}$. A correction must, however, be introduced, because the H_2SO_4 liberated combines with some of the Na_2SO_4 to give bisulphate. Special experiments were carried out to measure this; it was found to be accompanied by an absorption of heat, so that the total heat absorbed in the previous experiment had been too great. When the correction is applied it is found that $\frac{c_{\text{corrected}}}{a - b} = \frac{2}{3}$ approx., or that HCl has appropriated $\frac{2}{3}$ of the base, leaving $\frac{1}{3}$ to the H_2SO_4. So that under the same conditions exactly, HCl is twice as strong as H_2SO_4.

Ostwald's Volume Method.—A solution of copper nitrate[1] had a volume 3847·4 c.c., and an equivalent solution of copper sulphate had a volume 3840·3 c.c. Solutions of nitric and sulphuric acids had respectively the volumes 1933·2 c.c. and 1936·8 c.c. If no action occurred on mixing the $CuSO_4$ solution with the HNO_3 solution, the total volume would be $3840·3 + 1933·2 = 5773·5$ c.c.; if *complete* transformation into copper nitrate and H_2SO_4 took place, the total final volume would be $3847·4 + 1936·8 = 5784·2$ c.c. The actual volume found after mixing $Cu(NO_3)_2 + H_2SO_4$ solutions was 5780·3 c.c., and by mixing the $CuSO_4 + HNO_3$ solutions, 5781·3 c.c. The mean of the two (they should be identical if disturbing effects such as formation of acid salts were absent) is 5781·0 c.c. If *complete* transformation from $CuSO_4 + HNO_3$ into $Cu(NO_3)_2 + H_2SO_4$ had taken place, the volume increase would have been $5784·2 - 5773·5 = 10·7$ c.c. The observed volume increase was $5781 - 5773·5 = 7·5$ c.c. Hence there is a preponderating amount of $Cu(NO_3)_2$ formed, or, in other words, HNO_3 is a stronger acid than H_2SO_4 in the ratio of 7·5 : 3·2; or nitric acid takes 70 per cent. of the base and sulphuric 30 per cent. Corrections analogous to those introduced into the thermo-chemical method alter this numerical result, the final values being that HNO_3 takes 60 per cent. of the base, H_2SO_4 40 per cent.

Ostwald's volume method is also applicable to the direct determination of $\frac{x}{1 - x}$ for *weak* acids, and hence allows of verification of the relationship already obtained, since the numerical values of k_1 and k_2 can be obtained independently. This was carried out by Arrhenius, the following table containing a few of his results.

Distribution Ratio of a Base between two Acids. (Observations of Ostwald, 1878; theoretical calculation by Arrhenius, *Zeitschr. phys. Chem.*, **5**, 14, 1890):—

---

[1] The data are quoted from Walker's *Introduction to Physical Chemistry*.

	Observed Value.[1]	Calculated Value.
$HNO_3 : CHCl_2COOH$	0·76	0·70
$HCOOH : CH_3COOH$	0·76	0·77
$HCOOH : C_2H_5COOH$ . . .	0·79	0·81
$CH_3COOH : C_3H_7COOH$ (normal acid)	0·53	0·53
$CCl_3COOH : HCOOH$	0·97	0·96
$CCl_3COOH : Cl_2CHCOOH$ . . .	0·71	0·70
$CCl_3COOH : CH_2ClCOOH$ . . .	0·92	0·92

Further, if strong acids possessed dissociation constants, the numerical values of such constants would be large, since large dissociation means a large value of k. Hence, when dissociation constants do not exist, an approximate idea of relative strength may be obtained from equivalent conductivity, since this gives a measure of α, the term Λ_∞ being very nearly the same for all acids. Another method would be by comparison of the catalytic power of various acids upon a reaction sensitive to $H^{\cdot}$ ion. That these effects are really proportional to one another was shown by Arrhenius. In the following table are given values of the equivalent conductivity and catalytic power referred to HCl set equal to 100. The relative avidity of any two acids, *i.e.* the value of $\frac{x}{1 - x}$, is simply the ratio of the equivalent conductivities or catalytic effects of the acids considered.

Acid.	Velocity Constant of Catalysed Reaction.	Equivalent Conductivity.
Hydrochloric . .	100	100
Nitric . . .	96	99·6
Sulphuric . . .	54	65·1
Oxalic . . .	18	19·7
Acetic . . .	0·4	0·4

HYDROLYSIS.

In the foregoing study of solutions we have regarded the water as simply inert. In reactions known as hydrolytic reactions water takes a stoicheiometric part in virtue of its ions $H^{\cdot}$ and OH', which are present in extremely small but nevertheless, for certain cases, not negligible quantities. The electrolytic dissociation of water takes place according to the reaction:—

$$H_2O \rightleftarrows H^{\cdot} + OH'.$$

It is thus quite analogous to the dissociation of a weak electrolyte.

---

[1] These numbers denote the fraction of the base taken by the stronger acid, *i.e.* the acid first mentioned. Thus HNO_3 takes 0·76 of the base, $CHCl_2COOH$ getting 0·24 of the base.

The Ostwald constant in this case should be:—

$$k = \frac{[H^\cdot][OH']}{[H_2O]}$$

where the terms in brackets denote equilibrium concentration values, and k is the true dissociation constant of water. Since, however, in water by itself, or in dilute solutions in general, the concentration of the water molecules is sensibly constant, it is customary to transfer this constant term $[H_2O]$ into the term k, and write as the so-called dissociation constant of water, or better "the ionic product":—

$$K_w = [H^\cdot][OH'].$$

In pure water, or absolutely neutral solutions of salts, obviously $[H^\cdot] = [OH']$, and we find for such cases that the concentration of either ion $= \sqrt{\text{ionic product}}$. As will be shown later, the numerical value for the concentration of either H˙ or OH′ in neutral solution is 1×10^{-7} gram-moles per liter. K_w is therefore of the order 10^{-14}.

We might now consider for a moment the ordinary dissociation of a weak acid—say, acetic acid, taking into consideration the dissociation of the solvent. According to the ordinary form of Ostwald's Dilution Law—

$$k_{\text{acid}} = \frac{[H^\cdot][A']}{[HA]} \quad . \quad . \quad . \quad . \quad (1)$$

That is to say, in the aqueous solution of this acid we have the concentration of H˙ ion possessing the value $[H^\cdot]$, which is in general considerably larger than 10^{-7} gram-moles per liter, its value in pure water. But since we are considering a dilute solution, it follows that simultaneously we must have the following relationship satisfied:—

$$K_w = [H^\cdot][OH'] \quad . \quad . \quad . \quad . \quad (2)$$

Since $[H^\cdot]$ is much greater than 10^{-7} moles per liter, and K_w is constant, it is obvious that $[OH']$ is much less than 10^{-7}.

Further, since the system is on the whole electrically neutral, it follows that the sum of the (+) ions = the sum of all the (−) ions.

Therefore $$[H^\cdot] = [OH'] + [A'] \quad . \quad . \quad . \quad . \quad (3)$$

that is $$[H^\cdot] = \frac{K_w}{[H^\cdot]} + \frac{k_{\text{acid}}[HA]}{[H^\cdot]}$$

or $$[H^\cdot]^2 = K_w + k_{\text{acid}}[HA].$$

This is the strictly accurate form of the dissociation or dilution law. K_w, however, is in general negligible compared to $k_{\text{acid}} \times [HA]$, *e.g.* in a normal solution of acetic acid $[HA]$ is practically unity, owing to the small dissociation of the acid, $k_{\text{acid}} = 1{\cdot}8 \times 10^{-5}$, while K_w is much smaller, *viz.* $1{\cdot}2 \times 10^{-14}$. Neglecting K_w in the above expression, we get—

$$[H^\cdot]^2 = k_{\text{acid}}[HA]$$

or $$k = \frac{[H^\cdot]^2}{[HA]}$$

which is the ordinary form of Ostwald's Dilution Law. We have not yet dealt, however, with a hydrolytic reaction. The phenomenon of hydrolysis comes in when *we are dealing with a solution of a salt* (*not* the acid or base by itself), the acidic or basic or both components of which salt are *weak*. Let us consider a solution of sodium phenate. It dissociates into the ions—

$$C_6H_5ONa \rightarrow C_6H_5O' + Na^{\cdot}.$$

Sodium hydroxide is, of course, a strong base, and it must be borne in mind that almost all salts dissociate very largely, whether their constituents are strong or weak. In, say, a normal solution of the above salt, we have thus "momentarily" a very large concentration of C_6H_5O' ions, probably 0·75 N. Now phenol is an acid which dissociates according to the equation—

$$C_6H_5OH \rightleftarrows C_6H_5O' + H^{\cdot}$$

and the dissociation constant $\dfrac{[C_6H_5O'][H^{\cdot}]}{[C_6H_5OH]}$ is only $1 \cdot 3 \times 10^{-10}$ which means that only an extremely small quantity of C_6H_5O' ions can exist in presence of $H^{\cdot}$ without uniting to give undissociated C_6H_5OH. As a matter of fact, in the above case of sodium phenate solution, which "momentarily" gives rise to almost normal concentration of C_6H_5O' ions the concentration of $H^{\cdot}$ from the solvent is too great to allow these ions to remain uncombined with one another—since they must conform to the equation giving $1 \cdot 3 \times 10^{-10}$ as the dissociation constant of the acid. What happens is that undissociated C_6H_5OH is formed, thereby using up $H^{\cdot}$ and C_6H_5O' simultaneously, until the expression—

$$\frac{[H^{\cdot}] \times [C_6H_5O']}{[C_6H_5OH]}$$

has attained the necessary value. But the disappearance of $H^{\cdot}$ necessarily means the further production of OH' ions from the water, since the product of $[H^{\cdot}][OH']$ is constant, and hence the solution as a whole reacts *alkaline*—alkalinity being due to excess OH'. This is the mechanism based on the theory of electrolytic dissociation to account for the alkalinity of solutions of sodium phenate. The same behaviour is exhibited by sodium carbonate or KCN solutions, because CO_2 and HCN are extremely weak acids. In the case in which we deal with a solution of a salt containing a weak base—say, aniline hydrochloride, or $AlCl_3$—the resultant reaction is acid, for here the OH' of the water is used up in combining with the $Al^{\cdots}$ ions to give some undissociated $Al(OH)_3$, which is so weak a base, *i.e.* possesses so small a dissociation constant, that the product of the $Al^{\cdots}$ ions and OH' ions in the present case would exceed the necessary value for equilibrium, and since $[H^{\cdot}] \times [OH']$ is always constant, it follows that more $H^{\cdot}$ is produced from the water, as OH' is used up to form $Al(OH)_3$, and $H^{\cdot}$ remains in the solution as such, thereby giving the acid reaction. A very interesting case now presents itself, *viz.* a solution of a salt made up of two weak components, *e.g.* aluminium acetate, aniline acetate, or ammonium acetate. In this case $H^{\cdot}$ ion is removed from the solution along with acetanion to give some undissociated CH_3COOH. Simultaneously OH' is removed from the solution along with NH_4 or $Al^{\cdot\cdot\cdot}$, to give undissociated NH_4OH or $Al(OH)_3$, and therefore, although the extent of the hydrolysis is very great, the solution is not so acid or so alkaline as in the previous cases. In fact, *if the dissociation constants of the acid and the base were identical, we would have hydrolysis, and yet the solution would be neutral.* The student must therefore be on his guard against assuming that presence of neutrality means absence of hydrolysis. This case, however, is extremely rare; and whenever acidity or alkalinity exhibits itself in a solution of a salt we can infer hydrolysis.

The earlier manner of representing a hydrolytic reaction was as follows:—

$$KCN + H_2O = \underset{\substack{\text{Completely}\\\text{dissociated.}}}{KOH} + \underset{\substack{\text{Practically}\\\text{undissociated.}}}{HCN}$$

There is here excess OH' and hence the solution reacts alkaline.

Or again $$AlCl_3 + 3H_2O = \underset{\substack{\text{Practically}\\\text{undissociated.}}}{Al(OH)_3} + \underset{\substack{\text{Largely dissociates.}\\\text{Hence large amount}\\\text{of H}^{\cdot}\text{ and therefore}\\\text{acid reaction.}}}{3HCl}$$

In this particular case, however, it is probable that we have progressive hydrolysis (Denham, *Trans. Chem. Soc.*, **93**, 42, 1908).

The mechanism of the reaction, however, in all cases involves the ions of water rather than the undissociated molecules of water. The above method of writing the reaction though convenient, is erroneous. It will be seen that the essential thing about hydrolysis is the formation of one or more undissociated products, and this depends on the weakness of the acid and basic constituents. In the case of NaCl solution, for example, hypothetical hydrolysis might be represented by—

$$NaCl + H_2O = NaOH + HCl,$$

but BOTH the acid and base are practically completely dissociated, *i.e.* there is a large and equal quantity of $H^{\cdot}$ and OH', and the product is much greater than K_w, and hence there is a combination of these ions, leaving the solution neutral, and no undissociated acid or base exists. The reaction may be represented in the ordinary way—

$$NaCl \rightleftarrows Na^{\cdot} + Cl'.$$

We now turn to the question—

How does the extent of the hydrolysis vary with the dilution of the system?

CASE I.—Let us take the case of a salt consisting of a *strong acid* and *weak base* or *vice versâ*. Adopting the older notation the reaction is either—

$$AB + H_2O = \underset{\substack{\text{Practically}\\ \text{undissociated.}}}{BOH} + \underset{\substack{\text{Largely}\\ \text{dissociated.}}}{HA}$$

or

$$AB + H_2O = \underset{\substack{\text{Largely}\\ \text{dissociated.}}}{BOH} + \underset{\substack{\text{Practically}\\ \text{undissociated.}}}{HA}$$

Applying the law of mass action to the above stoicheiometric equation, we obtain—

$$\frac{[BOH] \times [HA]}{[AB] \times [H_2O]} = \text{constant},$$

and since $[H_2O]$ is constant,

$$\frac{[BOH] \times [HA]}{[AB]} = \text{a constant, called the } \textit{hydrolytic constant}.$$

Suppose we have dissolved 1 mole of salt AB in v liters of water and x is the fraction hydrolysed, then—

$$\frac{x^2}{v^2} \cdot \frac{v}{1 - x} \text{ or } \frac{x^2}{(1 - x)v} = \text{constant},$$

so that as v increases so must x, *i.e. the hydrolysis increases with the dilution*. It must be observed that this conclusion is not always true (see Case II.). The only sound treatment is to consider the effect from the standpoint of ions, for hydrolysis only exists in virtue of the fact that water gives rise to the ions $H^{\cdot}$ and OH'.

We shall therefore look at the question from the standpoint of the ions of water rather than the undissociated molecules. Let us take as a specific case the hydrolysis of KCN.

If we start with 1 mole of KCN in v liters we find at equilibrium the concentration terms are as follows:—

$$\frac{x}{v} \text{ moles per liter HCN} + \frac{x}{v}\text{KOH} + \left(\frac{1 - x}{v}\right)\text{KCN}.$$

Neglecting the dissociation of HCN (especially in presence of CN' ions from the completely dissociated KCN; the CN' concentration $= \left(\frac{1 - x}{v}\right)$, we may put the concentration of *undissociated* HCN as $\frac{x}{v}$.

From the ionic product of water we have

$$K_w = [H^{\cdot}][OH'] \text{ or } [H^{\cdot}] = \frac{K_w}{[OH']} = \frac{K_w}{\frac{x}{v}}$$

because the KOH present is completely dissociated, and this is the main source of the OH' ions.

Further, writing the dissociation constant of the acid as k_a,

we find $$k_a = \frac{[H^{\cdot}][CN']}{[HCN]} = K_w\frac{(1 - x)v}{x^2}.$$

Hence
$$\frac{K_w}{k_a} = \frac{x^2}{(1 - x)v}.$$

Denoting the hydrolytic constant by $\frac{x^2}{(1 - x)v}$, it follows that the hydrolytic constant $= \frac{K_w}{k_a}$.

It will thus be seen that the hydrolytic constant is greater the smaller is k_a, *i.e.* the weaker the acid. For HCN $k_a = 1{\cdot}3 \times 10^{-9}$ and $k_w = 1{\cdot}2 \times 10^{-14}$.

Solving for x in the above equation, we get

$$x = \frac{-vK_w}{2k_a} \pm \sqrt{\frac{v^2}{4}\left(\frac{K_w}{k_a}\right)^2 + \frac{vK_w}{k_a}}.$$

In the cases in which $\frac{K_w}{k_a}$ is small compared with unity, *i.e.* when k_a is considerably larger than K_w, the expression reduces to

$$x = \sqrt{\frac{vK_w}{k_a}},\ i.e.\ x \propto \sqrt{v} \text{ as before.}$$

The hydrolysis of a salt consisting of *one* weak constituent can be calculated if we know the ionic product of water and the dissociation constant of the weak constituent.

ILLUSTRATION.—HYDROLYSIS OF POTASSIUM CYANIDE, KCN.
(Shields, 1893.)

Concentration of KCN in Moles per liter $= \frac{1}{v}$.	Fraction of each Mole of KCN Hydrolysed.	$\frac{x^2}{(1 - x)v}$.
0·947	0·0031 or 0·31 per cent.	$0{\cdot}9 \times 10^{-5}$
0·235	0·0072 ,, 0·72 ,,	$1{\cdot}22 \times 10^{-5}$
0·095	0·0112 ,, 1·12 ,,	$1{\cdot}16 \times 10^{-5}$
0·024	0·0234 ,, 2·34 ,	$1{\cdot}3 \times 10^{-5}$
		Mean $1{\cdot}1 \times 10^{-5}$

CASE II.—Now consider the hydrolysis of a salt containing *both* a weak acid and weak base, *e.g.* urea acetate or aniline acetate. If we start with 1 mole of the salt in v liters, and a fraction x is hydrolysed, then the equilibrium corresponds to $\frac{1 - x}{v}$ moles of salt practically completely dissociated,

$$i.e.\ \frac{1 - x}{v} = \text{the concentration of } A' \text{ or } B^{\bullet}$$

likewise $\frac{x}{v}$ denotes the concentration of the acid (very slightly dissociated),

and $\frac{x}{v}$ moles base (very slightly dissociated).

We must take into account the dissociation constants k_a and k_b of the free acid and base. From the dissociation of water we have the relationship

$$[\mathrm{H}^{\cdot}][\mathrm{OH}'] = \mathrm{K}_w.$$

For the acid
$$\frac{[\mathrm{H}^{\cdot}][\mathrm{A}']}{[\mathrm{HA}]} = k_a.$$

For the base
$$\frac{[\mathrm{B}^{\cdot}][\mathrm{OH}']}{[\mathrm{BOH}]} = k_b.$$

Since the dissociation of the acid and base is very small, we may write the concentration of the undissociated acid thus:—

$$[\mathrm{HA}] = \frac{x}{v}, \text{ and similarly, } [\mathrm{BOH}] = \frac{x}{v}.$$

Hence
$$k_a = \frac{[\mathrm{H}^{\cdot}]\left[\frac{1-x}{v}\right]}{\frac{x}{v}}$$

and
$$k_b = \frac{[\mathrm{OH}']\left[\frac{1-x}{v}\right]}{\frac{x}{v}}$$

whence
$$k_a \times k_b = [\mathrm{H}^{\cdot}][\mathrm{OH}']\left[\frac{1-x}{x}\right]^2 = \mathrm{K}_w\left[\frac{1-x}{x}\right]^2.$$

In words, $\frac{\text{concentration of acid} \times \text{concentration of base}}{(\text{concentration of unhydrolysed salt})^2}$, which is expressed by $\frac{x^2}{(1-x)^2}$, is a constant, namely $= \frac{\mathrm{K}_w}{k_a k_b}$.

In such a case, therefore, when both constituents of the salt are weak the v term vanishes. That is to say, *the extent of the hydrolysis is independent of the dilution.* This behaviour is essentially different from that of the previous case, in which it was shown that x is proportional to $\sqrt{v}$.[1] The above conclusion was verified by Arrhenius and Walker in 1890 in the case of aniline acetate ("anilinium" acetate, compare Denham, *l.c.*).

---

[1] This result shows the error of ascribing hydrolysis to the water *molecule.* Had the latter been the effective agent we would have expected *even in Case II.* that the degree of hydrolysis should vary with the dilution.

v =	12·5	25	50	100	200	400	800	
$100x$ =	54·6	55·8	56·4	55·1	55·6	55·4	56·9	Mean 55·7

It has been recently pointed out by Tizard (*Trans. Chem. Soc.*, **97**, 2477, 1910) that the concentration of H$^\cdot$ ion and therefore of OH$'$ ion in a solution of a salt (made up of two *weak* constituents) is constant whatever the dilution may be. This is seen to be a necessary deduction from the equations given, for

$$k_a \qquad \frac{[\mathrm{H}^\cdot]\left[\dfrac{1 - x}{v}\right]}{}$$

or

$$[\mathrm{H}^\cdot] = k_a\frac{x}{1 - x} = k_a\sqrt{\frac{\mathrm{K}_w}{k_a k_b}} = \text{a constant.}$$

Experimental evidence in favour of this is put forward by Tizard, based upon colorimetric measurements. The addition of a few drops of aniline acetate solution to a neutral solution of methyl orange causes the same rise in colour as the addition of a large quantity of aniline acetate.

METHODS OF DETERMINING HYDROLYSIS AND THE HYDROLYTIC CONSTANT.

It might be thought that this would be a very easy matter, simply involving a titration of the excess H$^\cdot$ or OH$'$, but this is quite out of the question, for if we commence to neutralise, say, the free acid in the case of aniline hydrochloride, the equilibrium is disturbed and new equilibrium states are successively set up. This goes on until the whole of the HCl is neutralised. A solution of aniline hydrochloride, therefore, behaves towards alkali exactly like a solution of HCl of the same equivalent concentration. Exactly the same thing happens, say, in the case of Na_2CO_3 solution, which reacts alkaline owing to the free OH$'$. This cannot be titrated with acid, as otherwise the neutrality end point is only reached (using methyl orange as indicator) when the whole of the carbonate has disappeared as such, *i.e.* the solution behaves like an NaOH solution of the same equivalent concentration. It is evident that recourse must be had to some method of investigation which permits us to measure the hydrolytically produced H$^\cdot$ or OH$'$ without altering the equilibrium. The methods employed are essentially physical. The most important are—

(1) Measurement of the catalytic effect of the H$^\cdot$ or OH$'$ determined by the rate of inversion of sugar, decomposition of diazoacetic ester, hydrolysis of methyl acetate, or other catalysable reaction.

(2) Electrical conductivity measurements.

(3) Determination of the lowering of freezing point.

(4) Distribution of one of the products of hydrolysis of the partially hydrolysed salt between two solvents. (3) and especially (4) are typical instances of heterogeneous equilibrium, and will be considered later on.

(5) From electrometric measurements, *i.e.* measurement of the E.M.F. of cells fitted with hydrogen electrodes. From the values obtained one can determine the concentration of the $H^{\cdot}$ ion in a partially hydrolysed solution, and hence the extent of the hydrolysis. This will be taken up in the section on electrochemistry (Vol. II., Chap. VII.).

(6) Indirect methods: calculation of the hydrolytic constant from known values of K_w, k_a, k_b.

At present we shall only briefly discuss methods (1), (2), and (6).

(1) *Method based upon the inversion of Cane Sugar.*—H. Ley (*Zeitsch. physik. Chem.*, **30**, 222, 1899), employing this catalytic method, obtained the following values for the hydrolysis of $AlCl_3$, assuming a "first-stage" hydrolysis only, *i.e.* $AlCl_3 + H_2O \rightarrow AlCl_2OH + HCl$. Temperature 99·7° C.:—

v (Liters) Containing One Equivalent of Salt.	Velocity Constant k.	Per Cent. Hydrolysis $= 100x$.	Hydrolytic Constant $= \frac{x^2}{(1-x)v}$.
32	0·0422	8·04	$2{\cdot}2 \times 10^{-4}$
64	0·0346	13·2	$3{\cdot}14 \times 10^{-4}$
128	0·0258	19·7	$3{\cdot}78 \times 10^{-4}$
256	0·0185	28·2	$4{\cdot}33 \times 10^{-4}$
512	0·0136	41·4	$5{\cdot}71 \times 10^{-4}$

Ley knew by experiments with acid present alone what concentration of $H^{\cdot}$ ions corresponded to a certain velocity constant (k). Hence by simple proportion he was able to calculate the quantity of $H^{\cdot}$ ion which must have been present in the various salt solutions by observing the rate of inversion in the presence of these salts. Knowing the [$H^{\cdot}$ ion] we get the quantity of salt which must have undergone hydrolysis in order to produce this $H^{\cdot}$ ion. The source of error in the method is that the neutral salts themselves have probably a catalytic effect on the rate of inversion of the sugar, though to a much smaller extent than the $H^{\cdot}$ ion. It will be observed that the hydrolytic constant is not very constant, rising steadily as dilution increases. This may be ascribed to a second or even third stage hydrolysis coming in in the above case, *viz.*—

$$AlCl_3 + H_2O \rightarrow AlCl_2OH + HCl \text{ first stage}$$
$$AlCl_2OH + H_2O \rightarrow AlCl(OH)_2 + HCl \text{ second stage}$$
$$AlCl(OH)_2 + H_2O \rightarrow Al(OH)_3 + HCl \text{ third stage}$$

Ley carried out a similar series of experiments with many other metallic salts.

The determination of hydrolysis of salts by means of the catalytic saponification of the methyl acetate by means of H˙ ions follows exactly the same general principle as the above. One may also mention the extremely delicate catalytic reaction, *viz.* the decomposition of diazoacetic ester by means of H˙ ions (Bredig and Fraenkel, *Zeitsch. Elektrochem.*, **11**, 525, 1905) whereby [H˙] down to $\frac{N}{1000}$ are determinable, but the presence of neutral salts has a disturbing effect.

The following table (taken from a report by R. C. Farmer, *British Association Report*, 240, 1901) contains the values of the percentage hydrolysis of certain salts at decinormal concentration at 25° C. :—

HYDROLYSIS OF HYDROCHLORIDES OF WEAK BASES as measured by the catalytic decomposition of esters.

Base.	Per Cent. Hydrolysis.	Base.	Per Cent. Hydrolysis.
Glycocoll	19	Urea	90
Asparagine	25	Acetamide	98
Acetoxime	36	Thiourea	99

HYDROLYSIS OF ALKALI SALTS OF WEAK ACIDS as measured by the catalytic saponification of esters.

Acid.	Per Cent. Hydrolysis.	Acid.	Per Cent. Hydrolysis.
Hydrocyanic	1·12	p. chlorophenol	1·62
Acetic	0·008	p. cyanphenol	0·29
Carbonic	3·17	p. nitrophenol	0·16
Phenol	3·05		

HYDROLYSIS OF HYDROCHLORIDES OF WEAK ORGANIC BASES as measured by the rate of inversion of cane sugar.

Base.	Per Cent. Hydrolysis.	Base.	Per Cent. Hydrolysis.
Pyridine	1·2	Urea	81
Quinoline	1·2	Acetamide	78
Aniline	2·6	Asparagine	21

HYDROLYSIS OF THE CHLORIDES OF CERTAIN METALS as measured by the rate of inversion of cane sugar.

Base.	Per Cent. Hydrolysis.	Base.	Per Cent. Hydrolysis.
Zinc . . .	0·1 at 100° C.	Aluminium . .	2·7 at 77° C.
Lead . . .	0·2 ,, ,,	Cerium . . .	0·3 ,, 100° C.
Beryllium . .	1·8 ,, ,,	Lanthanum . .	0·1 ,, ,,
Aluminium . .	6·1 ,, ,,	Iron (Ferric) . .	10 ,, 40° C.

(2) *The Conductivity Method.*—If a salt—say, aniline hydrochloride—is hydrolysed to the extent x, then for a solution the total concentration of which is known and the specific conductivity of which is observed, the following relation holds, *viz.* :—

$$\Lambda = (1 - x)\Lambda \ + x\Lambda_{HCl}$$

where Λ stands for the apparent equivalent conductivity, *i.e.* the product of the *observed* specific conductivity into the volume containing one equivalent of the salt. The hydrochloric acid may be regarded as completely dissociated, and its conductivity is therefore constant. Such a solution does not obey Kohlrausch's Law for the mobilities of the ions. (In the above expression we have neglected the conductivity due to the practically undissociated base or basic salt formed by hydrolysis.) Solving for x in the above equation, one obtains—

$$x = \frac{\Lambda - \Lambda_v}{\Lambda_{HCl} - \Lambda_v}.$$

We can set Λ_{HCl}, the equivalent conductivity of HCl, at infinite dilution,[1] as equal to 383 at 25°. Λ_v stands for the equivalent conductivity the salt *would* have possessed had no hydrolysis taken place.

This can be evaluated by the method of Bredig (*Zeitsch. physik. Chem.*, **13**, 214, 1894), namely, by the addition of a sufficiently great excess of the free base to the hydrolytic salt solution until we reach the condition that—

$$\Lambda = \Lambda_v, \ i.e. \ x = 0$$

which must be obtained when Λ *observed has become independent of the quantity of free base added.* The applicability of this method obviously depends on the validity of assuming that the conductivity of the base itself is negligibly small compared with that of the salt. The following data are given by Bredig (*l.c.*) for the hydrolysis of aniline hydrochloride :—

The column headed Λ denotes the values of the equivalent conductivity when the solution is diluted with water only.

The column marked $\Lambda_v(32)$ denotes equivalent conductivity with $\frac{N}{32}$ aniline present in the solution.

---

[1] Strictly the HCl will not be in general completely dissociated, but no very serious numerical error is thereby introduced.

The column marked $\Lambda_v 64$ denotes values obtained with $\frac{N}{64}$ aniline present.

v.	Λ.	$\Lambda_v 32$.	$\Lambda_v 64$.
64	106·2	95·9	96·0
128	113·7	98·1	98·2
256	122·0	100·1	100·3
512	131·8	101·4	101·5
1024	144·0	103·3	103·3

The agreement between the two final columns shows that even with $\frac{N}{64}$ aniline present the hydrolysis of the salt has practically disappeared, for on increasing the aniline to $\frac{N}{32}$ the same value for Λ_v is obtained; the Λ_v in both cases being due simply to the two ions $C_6H_5NH_3^{\cdot}$ and Cl'.

By such means we obtain the value of Λ_v, *i.e.* the true equivalent conductivity of the unhydrolysed salt at dilution v, whilst the observed equivalent conductivity at the same dilution when hydrolysis actually occurs is given by Λ. The equation can thus be solved. The following data are given by Bredig (*l.c.*, p. 322) for the hydrolysis of aniline hydrochloride at 25° C.:—

v.	Λ.	Λ_v.	Per Cent. Hydrolysis $= 100x$.	$\frac{k_a}{k_w} = \frac{1}{K}$ (Hydrolytic Constant).
32	99·6	92·1	2·63	45×10^3
64	106·2	95·1	3·90	40×10^3
128	113·7	98·1	5·47	40×10^3
256	122·0	100·1	7·68	40×10^3
512	131·8	102·1	10·4	42×10^3
1024	144·0	103·1	14·4	42×10^3
				Mean 41×10^3

In the case of stronger bases than aniline their conductivity could not be neglected compared with Λ_v when v was large, *i.e.* at concentrations of base such as $\frac{N}{32}$ or $\frac{N}{64}$. In such cases more dilute solutions of the base have to be employed, for although the degree of dissociation of the base is greater the greater the dilution, the less is the absolute concentration of ions, and hence the less the effect upon the conductivity of the mixed salt and base.[1] It has been pointed out by Farmer (*Brit. Assoc. Report*, p. 240, 1901) that the conductivity method on the whole is not particularly accurate.

The Indirect Method (6).—We have already considered the methods of obtaining k_a and k_b, the dissociation constants of acid and base respectively. The determination of K_w, the ionisation constant for water, will be taken up later. Indeed, the degree of hydrolysis—measured by some one of the direct methods—has been employed as one of the means of calculating K_w. The values obtained by the direct methods (1 to 5) of determining hydrolysis, and therefore the hydrolytic constant yield values of K_w, which are in good agreement with those determined directly; and such agreement must necessarily be regarded as one of the most convincing pieces of evidence in favour of the theory of electrolytic dissociation.

THEORY OF INDICATORS.

An indicator is an electrolyte—essentially a weak acid or weak base—which gives rise to a colour change according as the solution into which it is introduced is made acid or alkaline. The action on the basis of the dissociation theory depends on the alteration produced in the degree of the dissociation of the indicator according to the amount of $H^{\cdot}$ or OH' present in the solution. The effectiveness depends on the property of a colour change accompanying the change in dissociation, that is, the undissociated molecule must possess a colour which differs from that of its ions, and the more marked the contrast is, the better, *ceteris paribus*, is the indicator. Since it is known that $H^{\cdot}$ and OH' themselves have no colour, an indicator which is a base, *i.e.* a basic indicator, must possess a coloured cation; an acid indicator must possess a coloured anion. The undissociated molecule must be either colourless, or differ in colour from the ion. The weakness of the indicator is essential, since the weaker it is the more will its dissociation depend on the variation of the $H^{\cdot}$ or OH' in the solution during the process of titration, and hence the sharper will the end point be. Very marked weakness alone, however, is not the deciding factor, as this in itself brings in certain effects, such as hydrolysis, to which reference will be made. As a typical acid indicator we may take phenolphthaleïn. This acid is extremely weak. The undissociated molecule is colourless. When completely dissociated, say, in the form of its sodium salt, the solution is bright pink, which must be due to the anion, since $Na^{\cdot}$ has no colour effect in the visible spectrum. In acid solution, *i.e.* in presence of relatively large $H^{\cdot}$ concentration, the dissociation of phenolphthaleïn will be thrown back so as to be practically undissociated, and hence the solution is colourless. In alkaline solution—excess of OH'—the $H^{\cdot}$ produced by the indicator acid will unite with OH' to give H_2O, and this process goes on until dissociation of the indicator is practically complete, and hence the solution is brightly coloured. Since the indicator is weak, a small drop of titrating acid or alkali will cause a sufficient change in the relative $H^{\cdot}$ and OH' concentration to cause the above marked colour change. As a typical basic indicator we may instance methyl orange. In alkaline solution the indicator is yellow, in acid, red. The yellow colour is due to the undissociated molecule, the red to the cation. Methyl orange contains a sulphonic acid group, which at first sight would lead us to think that this indicator is an acid one. That this is not the case, however, has been shown by Waddell (*Journ. Physical Chem.*, **2**, 171, 1897). The sulphonic acid group plays no part in the colour change. The significant group is the amido group in the molecule, $(CH_3)_2 . N . C_6H_4 . N_2 . C_6H_4SO_3H$, which adds on the elements of water just as ammonia does and yields a weak base. The writer is indebted to Prof. W. D. Bancroft for pointing out that further evidence in favour of regarding methyl orange as essentially a basic indicator rests on the fact that dimethylamidoazobenzene shows the same colour changes as methyl orange, although it contains no sulphonic acid group (Lunge and Marmier, *Zeitsch. angewandt. Chem.*, 1897). In alkaline solution the base will exist in the undissociated form, its molecule possessing yellow colour. In acid solution, say hydrochloric acid, the hydrochloride of the base will be formed, which being a salt will be largely dissociated into Cl^- (colourless) and $(CH_3)_2 . \overset{+}{N} : C_6H_4 : N . NH . C_6H_4SO_3H$ (red).

---

[1] The conductivity method in a modified form differing from that described has been employed by Walker (*Zeitsch. physik. Chem.*, 4, 333, 1889) to measure the hydrolysis of chlorides and sulphates of weak bases.

The problem may be looked at from the standpoint of relative avidity which we have considered. Suppose we start with a colourless solution containing some phenolphthaleïn in presence of the acid we desire to titrate. Caustic soda is added from the burette and distributes itself between the two acids present. We have seen that this distribution takes place (when the two acids are present in equivalent proportions) in the ratio of the square roots of their dissociation constants. Hence the advantage of phenolphthaleïn being very weak—it only gets a very small fraction of the base, and this inequality is still further increased by the fact that the concentration of the indicator is extremely small compared with that of the acid which is being titrated. If the indicator takes up the alkali, it of course dissociates, being now a salt, and the colour begins to appear. This, however, will be deferred until practically all the other acid has been titrated, *i.e.* converted into salt, and the production of colour, which must theoretically be a gradual process, only makes itself apparent within the limits of a small drop of alkali, *i.e.* within the limits of the accuracy of the titration. Exactly similar reasoning holds good in the case of methyl orange. Since phenolphthaleïn is the weakest acid indicator known, it is specially suitable for the titration of weak acids. It must be noted, however, when the indicator is phenolphthaleïn, that it is preferable to use a *strong* alkali as titrating agent, such as KOH or NaOH, not NH_4OH, so as to prevent hydrolysis, because the hydrolysis of a salt formed from a weak acid and weak base is much greater than that of a salt containing one strong component. Thus, suppose we had an acid solution, say, HCl, containing a little phenolphthaleïn, and were titrating it with ammonia, NH_4Cl (dissociated) is produced in large quantity, thereby driving back the dissociation of the ammonia itself, and therefore reducing the OH′ ions which should be free when the HCl is just neutralised. If this effect on the ammonia is marked, *i.e.* if there is much NH_4Cl present, it is quite conceivable that the OH′ produced by the drop of ammonia, even when the titration is complete, is scarcely great enough to cause the indicator to dissociate. In other words, the titration is not sharp. This is the same thing as saying that the ammonium salt of the indicator acid is largely hydrolysed, for hydrolysis in this case gives rise to a weak acid (the colourless phenolphthaleïn) and a weak base (NH_4OH) in large quantity, leaving a correspondingly smaller quantity of phenolphthaleïn *ion* (and $NH^{\cdot}_4$) present in the solution. On adding excess ammonia in the titration, therefore, the colour gradually appears, the addition of titrating agent required being now quite outside the limits of error inherent in making the determination, *i.e.* the burette reading. Hence the inaccuracy of the method. In the case of methyl orange as indicator, owing to the methyl orange being a weak base, the accuracy of titration is not so dependent on the strength of the titrating base.

Whilst methyl orange, functioning as a weak base, is moderately suitable for the titration of a weak base such as ammonia, methyl red is better. Methyl orange is quite unsuitable for the titration of a weak acid. Thus if we were titrating an alkali by means of acetic acid, and had reached the point at which the acetic acid was in slight excess, the salt of the indicator would then be formed, but owing to the weakness of both the acid and the base, the salt would be largely hydrolysed, so that the colour change (to the ionised red form) would only appear after an excessive quantity of acetic acid had been run in.

From the above considerations we may deduce the following rules. If we have to titrate—

1. Strong acid and strong base—use any indicator.
2. Strong acid and weak base—use a strong acid indicator or a weak basic one, *e.g.* nitophenol (acid), methyl orange.
3. Weak acid and strong base—weak acid indicator, *e.g.* phenolphthaleïn, litmus.
4. Weak acid and weak base—to be avoided.

Modification of the foregoing Theory of the Sensitiveness of Indicators.—The simple theory of Ostwald, in which the colour change is ascribed directly and entirely to change in ionisation of the indicator, has been shown to be not quite correct. On the new theory, an indicator, say an acid, in the undissociated form is a mixture of two or more tautomeric forms, HXO and XOH *in equilibrium.* Under suitable conditions the form XOH ionises, giving rise to the ions XO′ and H˙. The form HXO does not ionise of itself (see p. 264 *seq.*). The equilibrium equation of the whole indicator process is therefore—

$$HXO \rightleftarrows XOH \rightleftarrows XO' + H^{\cdot}$$

Owing to similarity in structure the individuals XOH and XO′ must be similarly coloured, $H^\bullet$ is colourless, and HXO being differently constituted to the other species present, may possess any colour or none. Thus HXO may be colourless, XOH and XO′ pink in equivalent solutions. When the indicator is placed in an acid solution its ionisation decreases, that is, XOH increases, and this in turn gives rise to more HXO, the solution thereby becoming colourless. On the other hand, if the solution is alkaline the dissociation of the indicator proceeds practically to completion. That is, the XOH concentration falls rapidly, and is made good at the expense of HXO, which then disappears, the solution becoming thereby pink, as in the case of phenolphthaleïn. If the solution were neutral it is conceivable that a colour midway between the two might be obtained. This is the case with litmus, in which the HXO form is bright red, the ions XO′ and the molecule XOH blue, the neutral solution being purple. Now ionic changes are instantaneous, the speed, therefore, with which an indicator changes its colour with changing acidity or alkalinity of the solution depends on the velocity of the tautomeric molecular change. A good indicator must possess the property of extremely rapid tautomeric change. Let us still further consider the case of an indicator which is a weak acid, its degree of dissociation being represented by α at the particular dilution investigated. Then applying Ostwald's Law we find that—

$$k_a \times \text{concentration of undissociated molecules} = C_{XO'} \times C_{H^\bullet}$$

or

$$k_a \,.\, \frac{1 - \alpha}{\alpha} = \text{concentration of } H^\bullet$$

where k_a is the dissociation constant of the indicator.

The degree of ionisation of an indicator, and therefore its colour, depends on the value of k_a and the $H^\bullet$ in the solution. Let us take a particular case. Suppose $\alpha = \frac{1}{2}$, then—

$$k_a = C_{H^\bullet}$$

That is, when the concentration of the $H^\bullet$ in the solution is numerically equal to the dissociation constant of the indicator, the latter is one-half ionised, and exhibits a colour midway between the two extreme colours corresponding to complete ionisation and zero ionisation respectively. Take another special case, *viz.*

$$C_{H^\bullet} = 10k_a.$$

Evidently here α must be 0·09 or 9 per cent. That is, the indicator is practically in the un-ionised state, and the colour will correspond to the un-ionised state. On the other hand, if $C_{H^\bullet} = \frac{1}{10}k_a$, then $\alpha = 0{\cdot}91$ or 91 per cent. The ionisation is now nearly complete, and the colour will be practically that corresponding to complete ionisation. Hence we arrive at the important conclusion that if we know the dilution of the indicator in a given solution, we can say at once within what limits of $H^\bullet$ the colour will change. That is, if we find that the indicator is showing a midway colour, we can say that the $H^\bullet$ ion in the solution lies between certain maximum and minimum values. For example, we can take a series of aqueous solutions containing $H^{\cdot}$ ion at the following concentrations: 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7} (neutral point at 25° C.), 10^{-8}, 10^{-9}, etc., equivalents per liter, and add small quantities of indicator to each. If methyl orange is the indicator, it will be found to be bright red in the 10^{-3} $H^{\cdot}$ solution, orange in the 10^{-4} $H^{\cdot}$, and yellow at 10^{-5} $H^{\cdot}$. We conclude, therefore, that its (basic) dissociation constant lies in the neighbourhood of 10^{-10}. Phenolphthalein is colourless in 10^{-7}, feebly coloured at 10^{-8}, and deeply coloured at 10^{-9}. Its dissociation constant lies, therefore, in the region of 10^{-8}.

The remaining considerations upon the subject of indicators are quoted from an article by H. T. Tizard (*British Assoc. Report*, 1911, p. 268).

"It is evident that if we wish to define with greater exactness the ranges of sensitiveness of indicators in this way we must measure as accurately as possible their dissociation constants. This, however, is by no means an easy task; an indicator is generally both too weak and too insoluble an electrolyte for us to be able to determine its dissociation constant by the ordinary conductivity method. The only accurate method appears to be a quantitative measurement of the depth of colour of the indicator in solutions of different, accurately known, concentration of hydrions. This is only convenient when the indicator is only coloured in one form or has two coloured forms which practically do not differ in tint, but only in depth of colour.[1] Approximate determinations made by means of the solutions already referred to are sufficient for most ordinary work, and it would be of the greatest assistance if in future every discoverer of a new indicator would test his product in this manner.

"Since the concentration of hydrogen ions in pure water is 10^{-7} at 25°, it follows that the exact neutral point is only indicated by an indicator with a dissociation constant of about 10^{-7} (litmus). It does not follow that this is the most useful indicator, in fact the contrary is true. Speaking generally, however, we may say that the most sensitive indicators are those which have dissociation constants not widely different from 10^{-7}; for evidently the change from 10^{-3} to 10^{-5} (methyl orange), that is from one-thousandth to one-hundredth-thousandth normal, is more considerable than the change from one-millionth to one-hundredth-millionth normal. An indicator must therefore be a weak acid or base, as Ostwald said. But it must not be too weak; an indicator with a dissociation constant of 10^{-11}, for example, changes over between concentrations of hydrogen ions of 10^{-10} and 10^{-12}, that is to say between concentrations of hydroxyl ions of 10^{-4} and 10^{-2} (since $C_{H^{\cdot}} \times C_{OH'} = 10^{-14}$ at 25°). Such a change is only brought about by addition of a considerable amount of alkali.[2]

---

[1] See *Trans. Chem. Soc.*, 1910, p. 2477.

[2] The range of sensitiveness of an indicator probably alters considerably with the temperature. The "apparent" dissociation constants of all pseudo-acids and bases have been found to have high temperature coefficients, and indicators should

"It is now possible to apply these conclusions to the actual process of titration. If an alkaline solution be gradually added to an acid solution, the concentration of hydrogen ions in the latter become smaller and smaller until a point is reached when the indicator present begins to dissociate appreciably. This point may or may not be the point when exactly equivalent quantities of base and acid are present together; that depends obviously upon the indicator used. Now we can either stop the titration directly we observe a distinct change in colour, or when further slight addition of alkali has no more appreciable effect. In practice it has been found most convenient to take as our end-point the *last* part of the colour change when we titrate from a dark to a light colour, and the *first* part of the colour change when we titrate in the reverse direction; and it is evident that, other things being equal, those indicators will give the sharpest and most satisfactory end-point which exhibit the greatest difference in depth of colour or tint between their two forms, because it is then an easy matter to detect a very small change in ionisation. Does the end-point depend upon the amount of indicator present? In the case of two-coloured indicators, such as methyl orange and methyl red, it does not, for we always titrate to a certain *fractional* change of the indicator. With mono-coloured indicators, such as phenolphthaleïn, it is different. In this case we go on adding alkali until there is a perceptible colour in the solution—that is to say, until there is a certain *amount* of coloured substance in the solution. If there is a large quantity of indicator present, this amount may be a very small fraction of it; if a small quantity, this amount may be a large fraction, and a glance at the equation—

$$k_a \times \frac{1 - a}{a} = \text{concentration H}^{\cdot}$$

will show that the smaller a is, the higher is the concentration of hydrogen ions indicated. A limit is, however, put on this by the insolubility of the indicator. In the particular case of phenolphthaleïn, the more indicator we use the more sensitive it is to small concentrations of hydrions, and the nearer is its 'end-point' to 10^{-7}, the theoretical neutral point. Owing to its insolubility, however, it is doubtful whether it can be used to indicate concentrations of hydrogen ions higher than $10^{-7.5}$.

"This influence of the amount of indicator present in the solution has not been sufficiently recognised, and may partly account for the

form no exception to this rule. If a 200th normal solution of acetic acid ($C_{H^{\cdot}} = 3 \times 10^{-4}$) containing methyl orange be warmed from 0° to 25 , the colour of the solution becomes distinctly paler, although the dissociation constant of acetic acid alters very little with the temperature, and in any case $C_{H^{\cdot}}$ does not become smaller. The phenomenon is best explained by an increase in the dissociation constant of methyl orange. It follows that when indicators are used for the colorimetric determination of hydrion concentrations, care should be taken to keep the temperature constant—a precaution which has not been thought necessary up to the present.

differences in the value for the end-point of phenolphthaleïn given by different observers.

"It may be remarked that it is possible for the amount of indicator present to affect the titration in another way. It has already been said that if a two-coloured indicator such as the basic one, methyl orange, is used, the titration is continued until a certain fraction of the indicator, say about 95 per cent., is changed over into the form of ions. Now this change, or neutralisation, of the indicator does actually require a certain definite amount of acid for its completion, and the more indicator is present the more acid will be needed. Most indicators of this class are, however, used in such dilute solution that this effect is negligible; and it is further important to notice that even if the concentration of the indicator is moderately high, the accuracy of the titration will not be affected if the indicator is originally put into the solution in the same form as it will have at the end of the titration. From this point of view, such an indicator as nitrophenol must be used in the form of its sodium or potassium salt.

"Bearing all these facts in mind it is possible to draw up a table showing the 'end-points' of various indicators when used in the ordinary manner in titration. Thus we have already seen that the colour change of methyl red is only complete when the concentration of hydrogen ions is something less than 10^{-6}; and the end-point observed when methyl red is used as an indicator in the ordinary manner lies somewhere between $10^{-5.7}$ and $10^{-6.4}$, the variation being relatively unimportant, and due to the inability of the eye to detect small changes in colour without a special apparatus. The following table gives the values of the end-points of the more common indicators; the actual numbers are probably not extremely accurate in some cases, but our knowledge is at present too imperfect to allow of their being defined with greater precision :—

Methyl orange	$10^{-4.5}$	to	$10^{-5.5}$
Methyl red	$10^{-5.7}$	„	$10^{-6.4}$
Litmus	$10^{-6.5}$	„	$10^{-7.5}$
Phenolphthaleïn	$10^{-8.2}$	„	10^{-9}
Thymolphthalein	$10^{-10.5}$	„	$10^{-11.5}$

"Having arrived at these numbers, all that remains is to consider how the concentration of hydrogen ions changes in a solution when we titrate acids and bases of various strengths. When we know this, we can not only decide upon the best indicator to use, but also estimate the probable error in using it, and the absolutely certain error in using any different one. If the acid and base used are both 'strong' electrolytes, for example, HCl and NaOH, then when equivalent quantities are present in solution we have an exactly neutral solution of an unhydrolysed salt (NaCl), and the concentration of hydrions will be exactly the same as in pure water, namely, 10^{-7} at 25°. Also, a very slight excess of acid and base makes an enormous difference in the concentration of hydrions in the solution. This can be seen most clearly by the accompanying curve, which represents the change in $H^{\cdot}$ ion concentration when the titration of 50 c.c. $^{N}/100$ HCl by $^{N}/100$ NaOH is almost complete. As ordinates are plotted the number of c.c. of base added; the abscissæ represent the concentration of $H^{\cdot}$ ions. When 49·95 c.c. of base are added the concentration of hydrions is 10^{-6}; when 50·05 are present, $C_{H}^{\cdot}$ is 10^{-8}; thus two drops of the alkali, or two parts in 1000 present, diminish $C_{H}^{\cdot}$ to 100th part. Along the curve are written in the various indicators at points which correspond to the 'end-points' they indicate. It will be seen that methyl red, litmus, phenolphthaleïn, coming as they do on the flat, or most sensitive part of the curve, all give sharp end-points, by which we mean that a small trace of the titrating solution is enough to make a sharp change in the colour. For methyl red about a drop of alkali is enough to decide its end-point; but the result so obtained (49·95 c.c.) may differ by about 1 part in 1000 from the true value. Phenolphthaleïn gives an equally sharp end-point, the error of which is a little over 1 part in 1000 in the other direction. We could therefore titrate with both in the solution, and take as the most correct result the mean of the two values obtained. For most purposes, however, an accuracy of 1 part in 1000 is ample. Methyl orange, however, comes on the steep part of the curve, and its colour changes comparatively slowly. Also the final result, which will be about 49·8 c.c., is considerably less accurate than those given by the other indicators used. Litmus should give the exact point; many workers find it, however, an inconvenient indicator to use; perhaps if its constitution could be determined, and a pure product prepared, it would again come into extensive use.

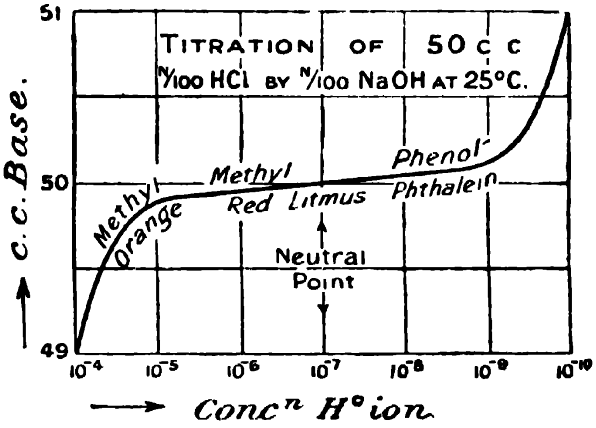


FIG. 46.

" Still more striking is the difference between the results obtained by using various indicators when one of the titrating liquids is a weak electrolyte. In this case, as is well known, the concentration of $H^{\cdot}$ ions in the solution when exact equivalents of acid and base are present is not the same as in pure water, owing to the hydrolysis of the salt, or, in other words, incomplete combination of the acid and base. Further, excess of acid or base does not alter the concentration of $H^{\cdot}$ ions to a large extent, since it is partly used up in destroying hydrolysis; also, if the weak electrolyte is in excess, the degree of its dissociation, small in any case, is further reduced by the presence of the neutral salt. Even in the titration of ammonia by HCl, and acetic acid by soda, where hydrolysis is as a matter of fact extremely small, and easily destroyed altogether by a slight excess of either constituent, we find that the flat part of the curve is much narrower and much less flat. Instead of there being a number of indicators which would give accurate results, we find only methyl red in one case, and phenolphthaleïn in the other. Methyl red gives not only an accurate but a sharp end-point in ammonia titrations;[1] phenolphthaleïn, instead of also giving an accurate result, gives an extremely inaccurate one, certainly not within 2 or 3 per cent. Methyl orange gives a better result in this case than phenolphthaleïn, but still not a sharp end-point. These facts have of course been long known, but the curves show well the magnitude of the errors involved —an important factor. In the titration of acetic acid by soda, methyl red gives an inaccurate and extremely bad end-point, phenolphthaleïn a sharp and accurate one. If the base or acid used is still weaker, it becomes very difficult to find a good indicator, and finally impossible; the flat part of the curve in fact tends to disappear until at last it does so altogether. As an example we can take *aniline*. Here, owing to the great hydrolysis of aniline hydrochloride in solution, the concentration of hydrions at the 'equivalent' point is as high as $10^{-3.5}$ and a large excess of acid or base produces only a slight change in this value. Since such concentrations of H˙ ions *do* actually affect the colour of methyl orange appreciably, it might be possible to titrate aniline to about 1 per cent. by using a comparison solution and a colorimeter,

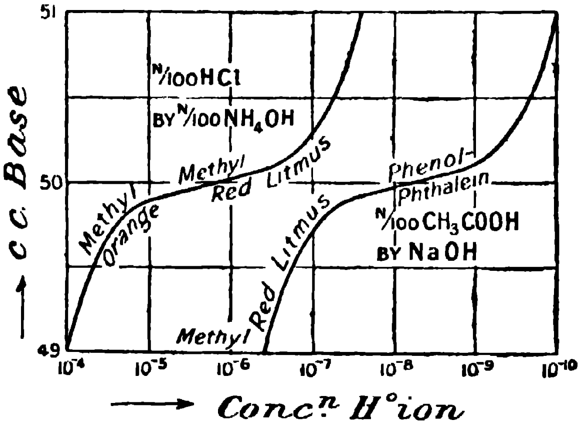


FIG. 47.

---

[1] E. G. Beckett (*private communication*) has found that this statement is only strictly true if the solutions be dilute. In the presence of large quantities of ammonium chloride, methyl red does not give as sharp an end-point as methyl orange, congo red, or eosin. It would appear from this that the flat part of the curve, Fig. 47, which in dilute solutions occurs at a concentration of 10^{-6} H ions, is displaced towards a region of higher acidity.

but evidently it is quite impossible to find an indicator capable of giving even moderately accurate results without this means.[1]

"A curve showing the titration of ammonia by acetic acid is also given: it will be seen that even though the concentration of hydrions at the 'equivalent' point is 10^{-7}, the curve is very nearly a straight line, and litmus is the only indicator that might possibly give moderately accurate results. But as it is never necessary to titrate a weak acid by a weak base, it is unnecessary to discuss this and similar cases further.

"The general conclusions to be drawn from the curves are these: firstly, that if we can find an indicator which will give a sharp and satisfactory 'end-point' in any particular volumetric operation, then the end-point so indicated will probably be accurate to within two parts in a thousand; secondly, that if no indicator will give a satisfactory end-point, then the only way to obtain really accurate results is to find an indicator the colour of which is sensibly affected at the concentration of hydrions obtaining in a pure solution of the salt of the strong and weak electrolytes, and then, using a comparison solution of the salt containing the same amount of indicator as the titrating solution, titrate to the same colour. In extreme cases results obtained by judging the colours with the unassisted eye will be too inaccurate, and a form of colorimeter should be used."

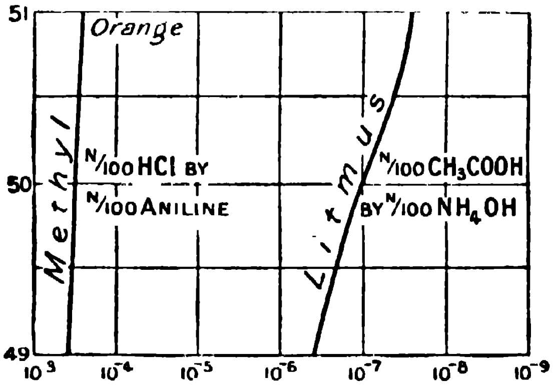


FIG. 48.

In connection with the use of phenolphthaleïn as an indicator the reader is referred to a paper by McBain (*Trans. Chem. Soc.*, **101**, 814, 1912), in which the sensitivity of this indicator is discussed especially in regard to the effect of carbon dioxide from the atmosphere.

---

[1] The concentration of hydrogen ions at the (true) end-point of a titration alters of course with the temperature, being in general about three times as small at 0° as it is at 25°. Reference to the curves given will show that this difference has very little effect on the probable accuracy of the titration, except when the acid or base titrated is extremely weak. It must be remembered that the effect is considerably lessened by a simultaneous decrease in the dissociation constant of the indicator.

Solutions of Reserve Acidity and Alkalinity (compare Washburn, *Journ. Amer. Chem. Soc.*, **30**, 36, 1908), from whose paper this account is mainly taken).

If a small amount of acid or alkali be added to pure water we know that there will be a corresponding marked change in the $H^{\cdot}$ ion and OH' ion content. The same is true of a solution of a neutral salt such as KCl. If, however, we use a solution containing a weak acid, say acetic acid, together with its salt, say sodium acetate, or a weak base together with its salt, we find that such a solution is by no means so sensitive to addition of acid or alkali as is pure water. In other words, such a solution possesses "reserve" acidity and alkalinity. Suppose we have a weak acid HA and its salt BA (the latter partly hydrolysed) together in a solution. Now let us add a small quantity of another acid, say HCl. The dissociation of the weak acid is thereby thrown back according to the equation—

$$A' + H^{\cdot} = HA.$$

Simultaneously the hydrolysis of the salt is thrown back owing to the reaction—

$$HA + OH' = H_2O + A'.$$

If the mixture is to be equally efficient in the removal of either $H^{\cdot}$ ion or OH' ion—according as an acid or an alkali is added to the mixture—it is evident from the above equations that the necessary condition is that HA should be equal to A′, that is,

$$[HA] = \gamma S \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where S is the total concentration of the salt BA and γ is its degree of ionisation. That is, for equal efficiency or equal reserve acidity and alkalinity, the mixture must be such that the concentration of the undissociated molecules of the weak acid shall be equal to the concentration of the anion A′ (produced almost entirely as a result of the dissociation of the salt BA). Let us assume that a given mixture of HA and BA is one of *equal* reserve acidity and alkalinity. For the ionisation of the weak acid we have—

$$K_a = \frac{[H^{\cdot}][A']}{[HA]} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$[H^{\cdot}] = \frac{[HA]}{[A']} \cdot K_a.$$

But in the case considered $[HA] = [A']$.

Hence, $\qquad [H^{\cdot}] = K_a.$

In words, in order to produce a solution of *equal* reserve acidity and alkalinity, it is necessary that the dissociation constant of the weak acid employed shall be identical with the $H^{\cdot}$ ion desired. For acetic acid, the dissociation constant is of the order 10^{-5}. Hence, by mixing sodium acetate and acetic acid in such proportions that $[HA] = [A']$, we shall obtain a solution of equal reserve acidity and alkalinity, the hydrogen ion concentration being of the order 10^{-5} gram-equivalents per liter. (Exactly similar reasoning holds good if we employ a mixture containing a weak base together with its salt.)

It follows from what has been said that, if we wish to prepare a *neutral* solution ($[H^\cdot] = [OH'] = 10^{-7}$ gram-equivalents per liter) with equal reserve acidity and alkalinity, it is necessary to employ a weak acid, the dissociation constant of which is 10^{-7}. In case no suitable acid can be found which exactly fulfils this condition, one is chosen which most nearly does so. Suppose its constant is

$$K_a = n[H^\cdot] \quad . \quad . \quad . \quad . \quad (3)$$

Then, if n is not too large, this acid can be used, provided the ratio of the salt [S] to the acid [HA] is changed. By combining equations (1), (2), and (3) the necessary ratio is given by the relation—

$$\frac{[S]}{[HA]} = \frac{n}{\gamma} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As convenient substances for this purpose we may take the two salts NaH_2PO_4 and Na_2HPO_4, the first functioning as the weak acid HA, the second as the salt BA. This is clear from the following considerations :—

The ionisation constants of the three dissociable hydrogens of phosphoric acid are—

$$\frac{[H^\cdot] \times [H_2PO_4']}{[H_3PO_4]} = 1 \times 10^{-2} \quad \text{(a strong acid).}$$

$$\frac{[H^\cdot] \times [HPO_4'']}{[H_2PO_4']} = 2{\cdot}1 \times 10^{-7} \quad \text{(a weak acid).}$$

$$\frac{[H^\cdot] \times [PO_4''']}{[HPO_4'']} = 5{\cdot}6 \times 10^{-13} \quad \text{(an extremely weak acid).}$$

The first hydrogen dissociation is that of a strong acid, but the salt of this acid, NaH_2PO_4, acts as a weak acid with the ionisation constant 2×10^{-7}, and is therefore suitable for the purpose in hand. The ionisation of the third hydrogen is negligible. We have therefore—

$[S] = C_{Na_2HPO_4}$, and $[HA] = [H_2PO_4'] = \gamma_1 C_{NaH_2PO_4}$, where $C_{NaH_2PO_4}$ is the total molar concentration of NaH_2PO_4, and γ_1 is its degree of ionisation, functioning as a salt. Substituting these values in equation (4) we find—

$$\frac{C_{Na_2HPO_4}}{C_{NaH_2PO_4}} = \frac{n\gamma_1}{\gamma}$$

and, since γ_1 can be assumed equal to γ, we conclude that the composition of the solution of *equal* reserve acidity and alkalinity, which is at the same time *neutral*, is given by the relation—

$$\frac{C_{Na_2HPO_4}}{C_{NaH_2PO_4}} = n = 2,$$

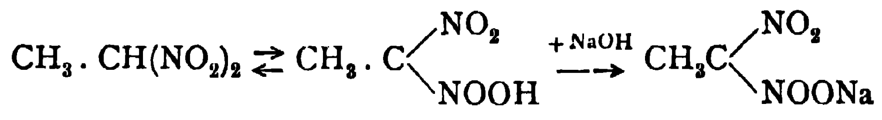
i.e. the solution must contain twice as much Na_2HPO_4 as NaH_2PO_4.

Naturally the magnitude of the reserve acidity and alkalinity depends upon the total amounts of the substances which go to form the solution. Washburn points out (*Principles of Physical Chemistry*, 1st ed., p. 328) that by means of the above mixture "it is possible to prepare a perfectly neutral solution which requires the addition of 0·5 equivalents of HCl per liter before it will show an acid reaction to Congo red, and which requires the addition of 0·5 equivalents of caustic soda per liter before it will exhibit an alkaline reaction to phenolphthaleïn. With distilled water, 5×10^{-5} equivalents of either reagent will be sufficient to change the indicator."

Washburn, in the paper referred to above, makes an interesting application of the principle of solutions of reserve acidity and alkalinity to the case of the iodometric determination of arsenious acid. The principle is also of importance for certain biochemical problems.

PSEUDO-ACIDS AND PSEUDO-BASES.

From the theoretical consideration of hydrolysis already given it will be evident that the possibility exists of calculating the strengths (*i.e.* the dissociation constants) of acids and bases the electrical conductivity of which may be too small to be determined directly in an accurate manner. This, however, depends essentially on the assumption that no intramolecular rearrangement takes place when the salts are formed. In certain cases, however, notably certain dyestuffs, indicators, etc., such changes do take place, *i.e.* the constitution of the salt is essentially different from the constitution of the acid. This is accompanied by several characteristic anomalies in behaviour. For example, Hantzsch found that such (sodium) salts, though formed from extremely weak acids, showed only *slight* hydrolysis. In the case of dinitroethane Hantzsch observed that both the acid itself and the Na salt were neutral, yet the possibility of an acidic form for dinitroethane is manifestly shown by the existence of a sodium salt; and further, this might be expected to be very largely hydrolysed. Hantzsch accounted for such behaviour by assuming the existence of a pseudo-acid form (the ordinary substance) which could change into a true acid form, and hence be capable of giving rise to a sodium salt. Since such a change is not necessarily instantaneous, the process of neutralisation by the alkali may—and is in many cases—a slow one. In the case of dinitroethane it may be assumed that we are dealing with the following series of changes:—



$$CH_3 . CH(NO_2)_2 \rightleftarrows CH_3 . C\left\langle\begin{matrix}NO_2\\NOOH\end{matrix}\right. \xrightarrow{+NaOH} CH_3C\left\langle\begin{matrix}NO_2\\NOONa\end{matrix}\right.$$

Pseudo form (gives rise to no salt). **True acid form.**

The following are examples of pseudo-acids and bases: nitroparaffins, nitroacetone, alkylnitrolic acids, oxythiazoles, cyanacetic amide, nitrosamines, oxyazo compounds, pyrazolones, oximes, oxamido ketones, nitrophenols.

The characteristics of pseudo bodies are :—

(1) Slow neutralisation (not present in all cases, however).

(2) Abnormally slight hydrolysis.

(3) No salt formation with NH_3 (or only very retarded formation) in benzene solution or any non-dissociating solvent.

(4) Salts coloured ; acid or base colourless or nearly so.

(5) Abnormal temperature coefficient of conductivity of the salt.

(6) Abnormal conductivity in aqueous-alcoholic or alcoholic solution, *i.e.* the conductivity is decreased in this solvent much more than in the case of true acids or true bases.

Hantzsch's theory is that we are dealing with tautomeric forms as in the case of dinitroethane. That this theory is not comprehensive enough is shown by the fact that it offers no explanation of the characteristic slight hydrolysis frequently noticed; for from the nature of the substance—even the tautomeric true acid or base—it is evident that we are dealing with weak bodies, and hence the salts formed from them should be extensively hydrolysed, which is not the case. For further information upon the subject of pseudo-acids and pseudo bodies generally, the reader should consult the *Annual Reports* issued by the Chemical Society during the last few years. For a purely dynamical view of pseudo-acids and bases which does not involve special " static " formulæ for the various coloured bodies obtained, the reader is referred to a paper by E. C. C. Baly, *Trans. Chem. Soc.*, 1915, p. 248.

AMPHOTERIC ELECTROLYTES.

Ostwald observed that the dissociation constant of amino-acids varied with the dilution. Wislicenus tried to explain it by polymerisation, but this was later shown to be incorrect. J. Walker, from 1904 onwards (*Proc. Roy. Soc.*, vols. **73** and **74**, 1904, and later volumes), was the first to investigate the matter thoroughly.

Consider an ordinary acid in solution. The ions present are—

	$H^{\cdot}$	OH'	X'	XH undissociated.
The equilibrium concentrations being	a	b	c	u respectively.

Then $ab = K_w$, where K_w is the ionisation constant of water.

$ac = k_a u$, where k_a is the Ostwald constant for the acid.

Also $a = b + c$ for electric neutrality.

$$\therefore a^2 = K_w + k_a u$$

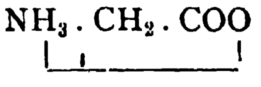
and neglecting K_w—

$a^2 = k_a u$ the ordinary Ostwald dilution expression.

Now take the simplest type of amino-acid, namely, glycollic acid, the formula of which is—

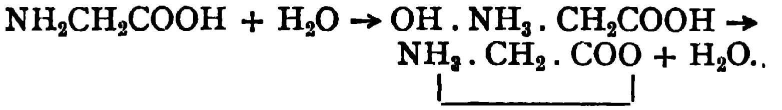
$$NH_2CH_2COOH.$$

This can give rise to an internal salt—



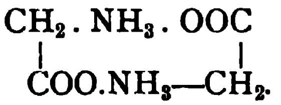
$$\underbrace{NH_3 . CH_2 . COO}$$

which naturally suggests the mechanism—



$$NH_2CH_2COOH + H_2O \rightarrow OH . NH_3 . CH_2COOH \rightarrow NH_3 . CH_2 . COO + H_2O.$$

It is also possible that external salt formation might take place between two molecules, *viz.*—

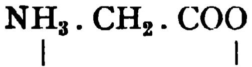


$$\begin{matrix} CH_2 . NH_3 . OOC \\ COO.NH_3—CH_2. \end{matrix}$$

That this, however, does not take place is shown by the fact that a molecular weight determination by the ordinary method leads to a normal value.

The un-ionised substances in solution are, therefore, the greater part of $NH_2 . CH_2 . COOH$ in equilibrium with its ions,

and



$$NH_3 . CH_2 . COO$$

and also a hydrated form, $OH . NH_3 . CH_2 . COOH$, which might be written in general $OH . X . H$.

Since this salt is formed by addition of water—

$$X + H_2O \rightleftarrows OHXH$$

in dilute solution, we can put—

$$[X] = k[OHXH]$$

or

$$\frac{[X]}{[OHXH]} = k,$$

since the concentration of the water is regarded as constant.

Besides OHXH in the un-ionised form, we have likewise ions produced from it, and this production can take place in two ways, *viz.*—an acid dissociation,

$$OHXH \rightarrow XOH' + H^{\cdot}$$

and a basic dissociation,

$$OHXH \rightarrow XH^{\cdot} + OH'.$$

There is also conceivably a reaction between the ions to give a salt, *viz.*—

$$(XH)^{\cdot} + (XOH)' \rightarrow 2X + H_2O.$$

The total ions and molecules in solution are therefore—

	$H^{\cdot}$	OH'	XOH'	$XH^{\cdot}$	HXOH	X
at the respective concentrations	*a*	*b*	*c*	*d*	*e*	*f*

These quantities are connected by the following equations :—

(1) $ab = K_w$ (ionisation constant of water).

(2) $bd = k'_b e$ (k'_b is the Ostwald constant of substance HXOH acting as a base, *i.e.*, "basic dissociation").

(3) $ac = k'_a e$ (k'_a is the Ostwald constant of HXOH acting as an acid, *i.e.* "acid dissociation").

(4) $cd = Qf^2$ from "salt formation" equation.

(5) $a + d = b + c$ for electrical neutrality of the solution as a whole.

Hence $abcd = k'_a k'_b e^2$ from (2) and (3);

also $abcd = K_w Q f^2$ from (1) and (4).

$\therefore K_w Q f^2 = k'_a k'_b e^2.$

$$\therefore \frac{e}{f} = \text{constant } \textit{independent of dilution.}$$

We have already seen this as a general phenomenon of hydrate or solvate compound formation (p. 186). It is clear that it is simply the inverted form of the previous expression—

$$\frac{[X]}{[OHXH]} = k.$$

Since $$\frac{e}{f} = \text{constant at all dilutions}$$

$$\frac{e+f}{e} = \text{constant at all dilutions.}$$

Setting $e + f = u$, the above equations may be rewritten—

(1) $ab = K_w.$

(2) $bd = k'_b e = k'_b (\text{const.} \times (e + f)) = k'_b (\text{const.} \times u) = k_b u.$

(3) $ac = k_a u.$

(4) $cd = Qf^2.$

(5) $a + d = b + c$ for electric neutrality.

We will now obtain alternate expressions for a, b, c, and d.

Since $$a + d = b + c$$

$$a + \frac{k_b u}{b} = b + \frac{k_a u}{a}.$$

$$\therefore a^2 + \frac{k_b u a}{b} = ab + k_a u.$$

Now $$ab = K_w.$$

$$\therefore a^2 + \frac{k_b a^2 u}{K_w} = K_w + k_a u.$$

or $$a^2\left(1 + \frac{k_b u}{K_w}\right) = K_w + k_a u$$

or $$a^2 = \frac{K_w + k_a u}{1 + \frac{k_b u}{K_w}}.$$

[Note that for ordinary acids the above equation would have been $a^2 = k_a u$.]

Also, since

$$ab = K_w$$

$$b = \frac{K_w}{a}$$

and since

$$ac = k_a u$$

$$c = \frac{k_a u}{a}.$$

Further, since

$$bd = k_b u$$

$$d = \frac{k_b u}{b} = \frac{k_b u a}{K_w}.$$

Now consider the special case of an amphoteric electrolyte whose basic dissociation constant k_b = the acidic dissociation constant k_a.

As before—

$$ac = k_a u$$

$$bd = k_b u$$

and since

$$k_a = k_b$$

it follows that

$$ac = bd.$$

$$\therefore \frac{b + c}{b} = \frac{a + d}{a}.$$

Also, since the solution is electrically neutral, it follows that—

$$a + d = b + c.$$

$$\therefore a = b, \text{ i.e. } [\text{H}^{\cdot}] = [\text{OH}']$$

and

$$c = d \text{ or } [\text{XOH}'] = [\text{XH}^{\cdot}].$$

The solution is therefore chemically neutral at all dilutions, since

$$\text{OH}' = \text{H}^{\cdot} = 10^{-7} \text{ gram-equiv. per liter.}$$

Again,

$$c = \frac{k_a u}{a} \qquad d = \frac{k_b u}{b} = \frac{k_b a u}{K_w}.$$

$$\therefore c + d = \frac{k_a u}{a} + \frac{k_a a u}{K_w}$$

$$\therefore \frac{c + d}{u} = k_a\left[\frac{1}{a} + \frac{a}{K_w}\right].$$

Now a has been shown to be constant at all dilutions.

Hence

$$\frac{c + d}{u}$$

is constant at all dilutions, *i.e.* the degree of dissociation of the amphoteric body is independent of the dilution.

Take as an example a substance with dissociation constants $k_a = k_b = 1{\cdot}2 \times 10^{-7}$ (at 25° C.).

It will be found that in this case the degree of dissociation is 52 per cent. at all dilutions. This means that a substance which is simultaneously an acid 100 times weaker than acetic and a base 100 times weaker than ammonia acts nevertheless as a fairly good electrolyte.

It is obvious from the foregoing consideration that the reason why those acids such as glycollic do not obey the simple Ostwald dilution law, is because that in addition to H' we have also another positive ion HX' having a different ionic velocity, and the quantity of this HX' is not negligible except as a limiting case. Thus for orthoaminobenzoic acid, with $k_a = 1{\cdot}04 \times 10^{-5}$ and $k_b = 1{\cdot}34 \times 10^{-12}$, the ratio of concentration HX' to H' at various dilutions is as follows:—

In liters v =	64	128	256	512	1024
$\frac{HX^{\cdot}}{H^{\cdot}}$	1·63	0·81	0·40	0·20	0·10

"Knowing[1] the concentration of the various ions and their ionic velocities, the molecular conductivity of the solutions can be calculated. Close concordance between the theoretical and observed results has been found with the 3 aminobenzoic acids, cacodylic acid, and asparagine." The (affinity) dissociation constants of a great many other amphoteric bodies have been measured (*cf. Chem. Soc. Report*, 1906, p. 20).

"The proper application of the theory of electrolytic dissociation has here explained away a class of apparent exceptions to the theory, the apparent divergence being due to an improper assumption, regarding the nature of the ions present" (Walker, *loc. cit.*).

In addition to organic amphoteric electrolytes, similar inorganic bodies also exist. Thus, take the case of aluminium hydroxide, $Al(OH)_3$. This will act as a base and neutralise an acid as in its reaction with hydrochloric acid. It will also act as an acid and dissolve in potash, giving potassium aluminate. If one assumes for simplicity that no intermediate stages exist, the *acidic dissociation* of aluminium hydroxide would be represented by—

$$Al(OH)_3 \rightarrow AlO_3''' + 3H^{\cdot}$$

and the *basic dissociation* by—

$$Al(OH)_3 \rightarrow Al^{\cdot\cdot\cdot} + 3(OH)'.$$

In a sense, water itself is an amphoteric substance, since it gives rise to H' and OH'.

THE IONISATION CONSTANT OF WATER.

As already frequently pointed out, the ionisation constant of water, K_w, is the product of the concentration in pure water of the two ions H' and (OH') in moles per liter. Though the numerical value of K_w is extremely small, *i.e.* of the order 10^{-14}, it has been found possible to measure it by several independent methods, the results of which are in satisfactory agreement. The following table gives a résumé of the attempts made to measure K_w, the method, and date.

---

[1] Walker, *Reports of the Chem. Soc.*, 1904.

$[H^{\cdot}]=[OH']$ in gram-moles per liter × 10^7.	Temp.	Author.	Date.	Method.
[6·0]	25	Ostwald, *Zeitsch. physik. Chem.*, **11**, 521.	1893	Conductivity of pure water.
[9·4]	?	Ditto.		Alkali and H_2 cell.
1·1	25	Arrhenius, *ib.*, **11**, 823. Shields, *ib.*, **12**, 184.	1893 „	Hydrolysis of sod. acetate, measured by ester saponification.
[0·1]	11	Wijs, *ib.*, **11**, 492.	1893	Saponification of methyl acetate by H_2O.
[6·0]	25	Bredig, *ib.*, **11**, 829. *Cf.* Arrhenius, *ib.*, **5**, 19, '90. *Cf.* Walker, *ib.*, **4**, 334, '89.	1893	Hydrolysis of aniline acetate from conductivity measurements.
1·2	25	Wijs, *ib.*, **12**, 514.	1893	Saponification of methyl acetate by H_2O.
0·8	18	Nernst, *ib.*, **14**, 155.	1894	Acid, alkali, H_2 cell.
1·05	25	Kohlrausch & Heydweiller, *ib.*, **14**, 330.	1894	Conductivity of pure H_2O.
1·2	25	Löwenberz, *ib.*, **20**, 293.	1896	Acid, alkali, H_2 cell.
0·91	25	A. A. Noyes & Kanolt, *Carnegie Inst. Pub.*, **63**, 297.	1907	Hydrolysis of ammonium-diketo tetrahydrothiazole by conductivity.
1·0	25	Hudson, *J. Amer. C. S.*, **29**, 1571 (1907); *ib.*, 1578 (1908). Circular No. 45, U.S. Dept. of Agriculture.	1909	Muta-rotation of glucose by acids and alkalies.

The methods may, therefore, be divided into—

(1) Direct conductivity of purest sample of H_2O.

(2) Catalytic effects of $H^{\cdot}$ and OH' in the saponification of methyl acetate; muta-rotation of glucose.

(3) From hydrolysis of salts, *e.g.* sodium acetate.

(4) Electromotive force measurements.

(5) There is also a method depending on the rate of change of conductivity of pure water with temperature which when compared with the heat of neutralisation of acids and bases affords strong grounds for supposing that the conductivity of pure water is due to $H^{\cdot}$ and OH' in certain proportions. It deals, however, more particularly with the change of K_w with temperature.[1]

The following is a slightly more detailed account of the above methods:—

---

[1] *Cf.* Heydweiller, *Ann. der Physik*, [4], **28**, 512, 1909.

(1) *Conductivity Method.*—Kohlrausch and Heydweiller determined the conductivity of water which had been freshly distilled *in vacuo* in platinum and sparingly soluble glass vessels, the specific conductivity observed at 18° C. being $0{\cdot}04 \times 10^{-6}$ reciprocal ohms.

Now this is due to the product of the number of ions ($H^{\cdot}$ and $(OH)'$) present into their mobility, *i.e.*—

$$0{\cdot}04 \times 10^{-6} = n \times (U + V) = n(318 + 174)$$

or $$n = \frac{0{\cdot}04 \times 10^{-6}}{492} = 0{\cdot}8 \times 10^{-10} \text{ gram ions per c.c.}$$

Hence concentration of $H^{\cdot}$ or OH' per liter is $0{\cdot}8 \times 10^{-7}$, and therefore—

$$K_w = [H^{\cdot}][OH'] = 0{\cdot}64 \times 10^{-14}.$$

(2) *Method of Methyl Acetate Catalysis.*—The saponification of methyl acetate may be represented—

$$CH_3COOCH_3 + OH' \rightarrow CH_3COO' + CH_3OH.$$

For every equivalent of OH' which thus disappears an equivalent of $H^{\cdot}$ must be formed, because their product is constant. Thus we have acetic acid produced which in the earlier stages of the reaction may be regarded as completely dissociated. Now separate experiments on the saponification of the ester by acids and alkalies have shown that the effect of OH' was 1400 times greater than that of $H^{\cdot}$. The effect of the $H^{\cdot}$ must be, of course, a purely catalytic one; that is, it probably by its catalytic power causes a water molecule to attack the ester, the $H^{\cdot}$ remaining at the same concentration throughout. The OH' is actually used up in the ordinary way as shown by the equation given above. If the process is as outlined, then, taking the case of ester in water, the decomposition starts with a certain velocity, which decreases owing to the disappearance of OH'. When the reaction is further advanced, however, the catalytic effect of the $H^{\cdot}$ begins to more than compensate for the diminishing OH', and the reaction constant begins to increase. It must, therefore, pass through a minimum. Wijs verified this directly by conductivity measurements (by measuring the rate of change of acetic acid formation per minute at different times).

Let us suppose the concentration of ester to be kept constant—this condition being practically fulfilled in the earlier stages of the experiment. Then the velocity of saponification is given by—

$$\frac{dx}{dt} = k_1[(OH)'] + k_2[H^{\cdot}]$$

where k_1 and k_2 are the velocity constants for saponification by OH' and $H^{\cdot}$ respectively at constant ester concentration. At the minimum velocity point, the rate of change of the velocity, *i.e.* $\frac{d}{dt}\left(\frac{dx}{dt}\right)$, must be zero, that is—

$$\frac{d^2x}{dt^2} = k_1\frac{d[\mathrm{OH'}]}{dt} + k_2\frac{d[\mathrm{H^{\cdot}}]}{dt} = 0 \quad . \quad . \quad . \quad (1)$$

Now, from the ionisation equation for water, it follows that—

$$[\mathrm{H^{\cdot}}][\mathrm{OH'}] = \mathrm{K}_w$$

and hence
$$\mathrm{H^{\cdot}}\frac{d[\mathrm{OH'}]}{dt} + [\mathrm{OH'}]\frac{d[\mathrm{H^{\cdot}}]}{dt} = 0 \quad . \quad . \quad . \quad (2)$$

must be fulfilled at any instant.

In order that (1) and (2) may simultaneously hold good, it is evident that—

$$\frac{[\mathrm{H^{\cdot}}]}{[\mathrm{OH'}]} = \frac{k_1}{k_2} \text{ which is known to be } = \frac{1400}{1}.$$

This value for the concentration ratio is the criterion for the minimum velocity point. Now it is necessary to determine the acetic acid produced at the minimum velocity point (say, by conductivity measurements). The acid was found to be of the order 10^{-6} normal at this point, and assuming complete dissociation of the acid, this gives us the actual [H$^{\cdot}$] and since we know that the OH$'$ is $\frac{1}{1400}$ of this, their product is easily calculated and hence K_w is obtained. The value obtained by Wijs in this manner is—

$$\mathrm{K}_w = 1·96 \times 10^{-14}.$$

K_w *from the Catalytic Muta-Rotation of Glucose* (Hudson, *Journ. Amer. Chem. Soc.*, **29**, 1571, 1907; *ibid.*, **31**, 1136, 1909).—Hudson measured the rate of change by means of the change of rotation in a polarimeter. The temperature was 24·7° C. The solution was made acid by HCl, thus furnishing a known amount of H$^{\cdot}$ ion. The following are a few of his figures:—

Concentration of HCl.	Polarimeter Reading at Time (in minutes).								
	0′.	5′.	15′.	25′.	35′.	45′.	60′.	∞.	*k*.
0 (water alone)	32·8	30·8	28·4	25·8	24·2	22·8	21·5	17·7	0·0106
0·001									0·0098
0·005									0·0112
0·10	31·4	27·0	23·7	21·9	20·4	19·6	—	17·8	0·0354

The velocity of rotation increases with increase in H$^{\cdot}$ ion. Osaka (*Zeitsch. physik. Chem.*, **35**, 702, 1900) found a similar relation in alkaline solution, but the catalytic effect of OH$'$ is much greater than that of H$^{\cdot}$ ion. Hudson finds the simple assumption to hold, *viz.* that simultaneous effect of both ions is simply additive, *i.e.*—

$$k = \mathrm{A} + \mathrm{B}[\mathrm{H^{\cdot}}] + \mathrm{C}[\mathrm{OH'}].$$

It will be noted that in very weak acid solution (0·001N HCl) k is less than that in pure water. The same phenomenon occurs in methyl acetate and is due to the same cause, *i.e.* depression of $[OH']$ owing to the presence in excess of the much less catalytically active $H^{\cdot}$ ion. The difference in catalytic effect is shown by the value of the constants B and C. Hudson found—

$$B = 0{\cdot}258,\ C = 9750.$$

In pure water, let the velocity constant of muta-rotation be k'_o, then—

$$k_o = A + (B + C)[H^{\cdot}],\ \text{for}\ [H^{\cdot}] = [OH'].$$

That is $[H^{\cdot}] = \dfrac{k_o - A}{B + C}$.

From Hudson's and Osaka's results A, B, C, and k_o are known, and hence the $[H^{\cdot}]$ can be obtained. The result is—

$$[H^{\cdot}] = 1{\cdot}0 \times 10^{-7}\ \text{gram ions per liter.}$$
$$\therefore K_w = 1{\cdot}0 \times 10^{-14}.$$

Hudson remarks that the accuracy of the method depends on the accuracy of determining the difference $k_o - A$, which in the case of glucose is not large, being only about 10 per cent. of the quantities themselves. Hudson considers the error in the result may be as much as 20 per cent. Experiments with fructose show that $k_o - A$ is much larger, and hence the result should be more accurate.

(3) *Method depending upon the Hydrolysis of Salts.*—It is necessary to determine the hydrolytic constant K_{hy}, say, of sodium acetate in water. Then K_w can be got from the relation $K_{hy} = \dfrac{K_w}{k_a}$, where k_a refers to acetic acid (see p. 245). Or we may proceed as follows:—

A solution of sodium acetate $\left(\dfrac{N}{10}\right)$ was found by Shields to be hydrolysed to the extent of 0·008 per cent., or the salt gives rise to 0·000008 mole per liter of acetic acid (practically undissociated in presence of much acetanion) and 0·000008 mole of NaOH completely dissociated, *i.e.* 0·000008 mole OH', or $[OH'] = 8 \times 10^{-6}$.

Now k_a for acetic acid $= \dfrac{[CH_3COO'][H^{\cdot}]}{[CH_3COOH]}$

and from separate experiments k_a is found to be $1{\cdot}78 \times 10^{-5}$. Now in the partially hydrolysed salt practically all the CH_3COO' present may be ascribed to the *salt*, which is practically completely dissociated (only an extremely small quantity of CH_3COO' is due to the acid). The concentration of $(CH_3COO)'$ may be put equal to 0·1 gram ion per liter.

$$\therefore [H^{\cdot}] = \frac{k_a[CH_3COOH]}{[CH_3COO']} = \frac{1{\cdot}78 \times 10^{-5} \times 8 \times 10^{-6}}{0{\cdot}1}$$
$$= 1{\cdot}42 \times 10^{-9}.$$

$$\text{Hence}\ K_w = [H^{\cdot}][OH'] = 1{\cdot}42 \times 10^{-9} \times 8 \times 10^{-6}$$
$$= 1{\cdot}136 \times 10^{-14}.$$

(4) *Electromotive Force Methods.*—These will be dealt with later (Vol. II. Chap. VII.).

(5) *Variation of* K_w *with Temperature.*—From a comparison of the variation of conductivity of the purest water with temperature (due to increased dissociation and increased mobility of the ions), with the heat of neutralisation of strong bases and acids, which is the heat of formation of water (or its heat of dissociation with reversed sign), Heydweiller has recently obtained the following values for K_w at various temperatures :—

$t°$ C.	0°.	10°.	18°.	25°.	50°.	100°.	150°.	200°.
$K_w \times 10^{14}$	0·116	0·281	0·59	1·04	5·66	58·2	234	525

This method cannot be gone into here in detail, because it involves a thermodynamic relation between K and Q, the heat of neutralisation, namely—

$$\frac{d \log K}{dT} = \frac{-Q}{RT^2}$$

(an expression known as the van 't Hoff isochore). It should be noted how very great is the temperature coefficient. On the basis of the above equation, Arrhenius calculated what the temperature coefficient of K_w would be, and predicted its remarkable magnitude (see Arrhenius, *Textbook of Electrochemistry*).

ELECTROLYTIC EQUILIBRIUM IN SOLVENTS OTHER THAN WATER.

This can only be briefly touched upon—chiefly because of the absence of any comprehensive generalisations. Many apparently contradicting phenomena have been observed, and the existence of such is the main argument advanced by the opponents of the Electrolytic Dissociation Theory.

It will be remembered that according to the Nernst-Thomson Rule, electrolytic dissociation of the solute and polymerisation of the solvent itself are connected with the dielectric constant of the solvent, a solvent of large dielectric constant giving rise to large dissociation of the solute. This is not always the case.

In general one finds—especially with regard to organic solvents—that electrolytic dissociation is much less than in the case of water. The determination of the degree of dissociation is, however, by no means an easy matter—the difficulty being to determine Λ_∞. Salts and " strong " acids or bases are not necessarily completely dissociated, even at great dilution, in many organic solvents, and, of course, may not be dissociated at all in many cases.

The value of α has, therefore, to be obtained by some other method, say, by lowering of freezing point or rise of boiling point, since the abnormal number of individuals present (if ionisation has taken place) is indicated by abnormal lowering of freezing point or rise of boiling point. These methods are not in general very accurate, and further, even in cases in which the accuracy is presumably fair, we meet occasionally with results which seem to prove that no dissociation has taken place, while at the same time the conductivity which the solutions possess is evidence that such must exist. Such facts, however, may be explained without giving up the principle of ionisation by considering the change in the polymerisation of the solvent which occurs simultaneously with changes in the molecular state of the solute. In fact, the most characteristic phenomenon in connection with non-aqueous solutions is the manifestation of solvent effects which only play a secondary *rôle* in aqueous solutions.

Sometimes, say, in the case of electrolytes in acetone, the molecular conductivity comes out much larger than the value at the same dilutions in water. Other evidence (cryoscopic, etc.) goes to show that the actual dissociation of the solute is considerably less than it is in water. This has been traced to the influence of the viscosity of the solvent. Thus the viscosity η of acetone is only about one-third that of water, and hence, to take a particular instance, the values of Λ_∞ of $AgNO_3$ in acetone comes out to be a number over 350, while in water it is only a little over 115.

One important generalisation which is at least approximately true in connection with Λ_∞ has been brought out as a result of the work of Dutoit, Friderich, Jones, Carrol, and Walden, namely, that Λ_∞ of a solute is inversely proportional to the viscosity of the solvent, or—

$$\Lambda_\infty \times \eta = \text{constant independent of solvent.}$$

Walden verified this relation in the case of tetraethyl-ammonium iodide when dissolved in a whole series of organic solvents, such as acetone, acetonitrile, ethyl chloride, methyl alcohol, nitromethane, acetic anhydride, benzaldehyde, furfurane, nitrobenzene, diethyl- and dimethyl-sulphate, formamide cyanacetic ester, etc. Further, Walden found this constant to be independent of temperature, which shows that the negative temperature coefficient of viscosity is numerically equal to the positive temperature coefficient of conductivity.

This generalisation can scarcely be regarded as very strictly accurate, for in many cases it is extremely difficult or impossible to determine Λ_∞, owing to the small degree of dissociation of solutes at ordinary dilution in organic solvents. That there is a connection at all between the conductivity of a solution and the fluidity of the solvent, *i.e.* the reciprocal of η, points to the supposition that the ions must be to a greater or less extent surrounded with an atmosphere of solvent molecules which they carry along with them, and hence their friction is the inner friction or viscosity of the solvent. We have already met with the phenomenon of hydration in the case of LiCl (notably) in water, as shown by the result of transport number determinations, and it appears that "solvation" in general, *i.e.* union of solvent and solute, frequently occurs.

From the above-mentioned results it is evident that solutes can exist in a partially ionised state in solvents other than water. Do these solvents themselves show any dissociation, even to a slight extent, such as occurs in the case of water? No definite evidence is forthcoming; if such exists the corresponding ionisation constants of the organic solvents must be still smaller than that of water. A further question is this. When reactions take place between substances, *i.e.* salts in organic solvents, does this presuppose ionisation?—in fact, do such reactions occur only between ions, or can undissociated molecules take part? Our experience with solutions in water is strongly in favour of the existence of ionisation as a necessary condition for chemical reaction, but in organic solvents this is more a matter of conjecture, though one is inclined to think that something of the kind takes place. The possibility that molecules can react must, however, be kept clearly in view—see, for example, the paper by Miss Burke and Donnan, on the interaction of alkyl iodides and silver nitrates (*Zeitsch. physik. Chem.*, **69**, 148, 1909), as well as the "Dual Theory" of Catalysis (Chap. IX.).

The Law of Mass Action (*the Dilution Law*).—The evidence as to whether this law holds or not in solvents other than water is conflicting. Thus Wakemann (*Zeitsch. physik. Chem.*, **11**, 49, 1893) found that for strong electrolytes in mixtures of ethyl alcohol and water the law did not apply, *i.e.* the behaviour is the same as in the case of water. Wilderman (*ibid.*, **14**, 247, 1894) found that in the case of trichloracetic acid (a strong acid) in absolute alcohol the dilution law held good. Carrara has found that the behaviour of methyl alcohol as a solvent is very similar to that of water. *i.e.* strong electrolytes disobey the law, weak electrolytes are in agreement with it. Rudolphi's Law holds, however, for strong electrolytes. Cohen (*Zeitsch. physik. Chem.*, **25**, 5, 1898), finding from the work of previous investigators, and likewise his own results, that neither the Ostwald Dilution Law nor that of Rudolphi held good in the case of a number of inorganic salts dissolved in ethyl alcohol and aqueous alcohol mixtures, comes to the conclusion that the ratio $\frac{\Lambda_v}{\Lambda_\infty}$ is not a correct measure of the degree of dissociation.

On the other hand, Godlewski (*Journ. de Chim. phys.*, **3**, 393, 1905) finds that for certain acids dissolved in ethyl alcohol and alcohol-water mixtures the dilution law holds good, the dissociation being calculated by the ratio $\frac{\Lambda_v}{\Lambda_\infty}$.

To show the influence of the gradual change in the nature of the solvent, the following data of Godlewski are given:—

(Godlewski investigated the behaviour of several acids other than salicylic and in general obtained similar results. The acids examined are weak (in aqueous solution)).

SALICYLIC ACID, 25° C.

Solvent per Cent. Alcohol.	Per Cent. Dissociation of $\frac{N}{64}$ Solution.	Dissociation Constant of Acid (Ostwald's Dilution Law) × 10^5.
0 {*i.e.* 100 per cent. H_2O	22·1	100·0
10	21·9	95·5
20	20·6	83·0
30	17·3	57·2
40	13·1	31·6
50	10·1	17·8
60	8·11	11·0
70	5·31	4·59
80	3·33	1·75
90	1·94	0·579
100	0·291	0·013

It may be noted that salicylic is one of the few acids which are fairly largely dissociated in *water*, *i.e.* at $v = 1024$ liters $\alpha = 62·8$ per cent., and yet it gives a dissociation constant.

Similar results were obtained with cyanacetic and bromacetic acids. Again, it has been shown that the maximal conductivities (*i.e.* the equivalent conductivities at infinite dilution) in the case of KI, NaCl, KCl, sodium salicylate, sodium cyanacetate, pass through a *minimum* value at 80 per cent. alcohol, the variation of Λ_∞ with alcohol content being observed over the range 0 to 100 per cent. alcohol. This suggests some kind of solvent complex formation which manifests itself in a viscosity-maximum of the solvent. That this maximum in viscosity, however, is not always the cause of the change in conductivity is shown by the work of Jones and his pupils in connection with certain salts dissolved in mixtures of water, methyl alcohol, ethyl alcohol, and acetone. Thus for $LiNO_3$ and $Ca(NO_3)_2$ a marked maximum in conductivity manifests itself in the case of the mixture acetone + ethyl alcohol (of certain composition), while the viscosity for varying compositions of mixed solvent is a straight line. This is ascribed by the authors to a change in the effective volume of the ions of the salt—the ions being solvated to different extents.

Kohlrausch's Law of the mobility of ions seems to break down in many cases in solvents other than water. Thus Carrara found that in methyl alcohol, as in water, the ions of the halogens and sodium and potassium have mobilities which are concordant when calculated from their different salts, NaCl, NaBr, KCl, KBr; on the other hand, when the salts contain the cations, NH_4, tetramethyl-ammonium, or sulfonium, the same anions appear to have different mobilities, *i.e.* the mobility does not appear to be independent of the salt from which it is produced.

For further study of non-aqueous solutions the following should be consulted:—

1. "Elektrochemie der nichtwäszrigen Lösungen," by G. Carrara; translated by K. Arndt (*Ahrens Sammlung*, **12**, 1907).
2. "The Present Status of the Solvate Theory," by H. C. Jones (*Amer. Chem. Journ.*, **41**, 19-57, 1909).
3. The work of P. Walden in the *Zeitsch. phys. Chem.*, from the year 1905 onwards.
4. The work of Hantzsch on H_2SO_4 as a solvent (*Zeitsch. phys. Chem.*, **61**, 297, 1907); also Bergius, *ibid.*, **72**, 352, 1910.

WATER AS A SOLUTE.

The following is a short abstract[1] of a paper by P. Walden, *Trans. Far. Soc.*, **6**, 71, 1910.

"We begin with the following three facts:—

"(1) The ionising power of a solvent stands directly in proportion to its dielectric capacity. This is the Nernst-Thomson rule. Walden's own experimental investigations on the molecular conductivity and on the degrees of electrolytic dissociation in non-aqueous solutions have given results which [in the main] are in accordance with this rule.

"(2) Water which forms polymerised molecules (Ramsay and Shields, etc.) [when alone], gives in all solvents—at small concentrations—only molecules of the form H_2O (Bruni and Amadori, *Trans. Far. Soc.*, **5**, 1910).

"(3) Water is also an electrolyte undergoing the electrolytic dissociation $H_2O \rightarrow H^{\cdot} + OH'$.

"At the present time we possess a great number of ionising organic and inorganic solvents, which are characterised by an extremely high dissociating power towards binary salts, and in accordance with this fact also, by very high dielectric constants. Such solvents are HCN (dielectric constant, $K = 95$), formamide ($K > 84$), H_2SO_4 ($K > 84$). These three solvents, therefore, possess a greater ionising power than water, because their dielectric constant is higher than that of water ($K = 80$). [Now the question arises] Is *water* a good conductor in such solvents?"

Walden found that the conductivity due to H_2O when dissolved in HCN is extremely small. Some of his data may be quoted.

Temp. = 0° C. Specific conductivity of pure HCN is $0{\cdot}657 \times 10^{-6}$ reciprocal ohms. The values given are corrected for this quantity. v stands for the dilution of HCN in liters which contains 1 mole of water.

v.	Specific Conductivity (corrected).	Equivalent Conductivity of Solution.
6·38	$0{\cdot}132 \times 10^{-6}$	0·00845
15·60	$0{\cdot}082 \times 10^{-6}$	0·0128
18·80	$0{\cdot}082 \times 10^{-6}$	0·015

---

[1] With some slight modifications, indicated thus [ ].

"When we compare the conductivity of the electrolyte water with the conductivity of a binary salt (say KI) in HCN as solvent, we perceive the enormous difference between these two electrolytes.

KI as Solute in Hydrocyanic Acid, T = 0° C.

v.	12·04.	27·07.	81·57.	
Λv	254	278	300	{ Kahlenberg and Schlundt.

v.	8.	16.	32.	
Λv	258	265	273	Centnerszwer."

Walden also found that H_2O dissolved in formamide and in formic acid is a very poor conductor. "On the other hand, we must accentuate the fact that formic acid with the lesser ionising power ($K = 58·5$) gives a higher conductivity [for dissolved water] than formamide with its greater ionising power (dielectric constant > 84). In nitrosodimethylamine, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>N—NO$, as solvent ($K = 53·3$) water scarcely conducts, and indeed conducts less than in formic acid, although the dielectric constants are practically the same and the viscosity of formic acid is about double that of the nitroso body. The results, therefore, lead to the following anomalous conclusions:—

"(1) Water dissolved in the solvents HCN, $HCONH_2$, HCOOH, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>N—NO$, shows in all these solutions very little conductivity.

"(2) The *smallest* numerical values of the conductivity were found in the solvents with the *highest* dielectric constant, and this further in spite of the great fluidity (for example in the solutions of HCN).

"(3) The highest values of the conductivity were observed in the solvent formic acid, which has a smaller fluidity and a smaller ionising power [*i.e.* slightly smaller K] than, for example, hydrocyanic acid.

"In the face of such results we must now ask the question: What is the cause of this anomalous behaviour of the water?

"Instead of a direct answer, we can only put forward an hypothesis. When all *physical* conditions were favourable to the existence of considerable electrolytic dissociation and great electrical conductivity of the solute, and nevertheless we have found small numerical values, then it seems to me [*i.e.* Walden] we must attempt a *chemical* interpretation of such anomalous results. Do they not stand in causal connection with the *chemical nature* of our solvents and water as the electrolyte? In short, is it not possible and probable that a body which is not *itself* an electrolytic conductor in the liquid state becomes, when dissolved, an electrolyte, if between this solute and the solvent there exists a *chemical* *contrast?* When such a contrast exists, the solute and the solvent will give a (more or less stable) molecular combination of a *salt character*.

"These conceptions are in agreement with the proposition of Hittorf, stated by him half a century ago (1859): 'All electrolytes are salts'. If we accept these views as a working hypothesis, we must conclude that water as an amphoteric body [$H^{\cdot}$ and OH' groups] will only become an electrolyte and a better conductor when it is dissolved in a liquid of a *distinctly acid or basic character*, that is, when it will form with this solvent a *kind of salt*."

This conclusion is amply borne out by experiment. We have already seen that formic acid as solvent dissociates water more than HCN or $HCONH_2$ as solvent, although the dissociation is still small in formic acid, *i.e.* Λ_v varies from 0·15-0·17 for $v = 2$ to $v = 21$. Employing H_2SO_4 as solvent, Bergius found the following values for the equivalent conductivity of H_2O dissolved:—

v.	1·88.	2·53.	6·9.	27·0 Liters.
Λ_v	17·8	54·7	56·6	73·4

"It is evident that only the strong acid solvents (H_2SO_4 and HCOOH) give a considerable conductivity to the dissolved water; the stronger the acid character of the solvent (*e.g.* H_2SO_4) the higher is the conductivity of the water." Although HCN has a very high dielectric constant and a very small viscosity, it is quite unable to ionise H_2O molecules because the solvent itself is almost neutral (being an extremely weak acid). Obviously these conclusions must hold good for the reversed case. Thus, if water is the solvent, the best conducting solutions ought to be those of H_2SO_4, the worst being those of HCN, because in the first case there is the marked chemical contrast which is absent in the second. As we have already seen, this is likewise borne out by experiment; HCN is one of the weakest acids when dissolved in water, giving a very small dissociation constant. H_2SO_4 in water is so strongly dissociated that it gives no constant at all. It must be pointed out that these conclusions of Walden really represent a considerable modification of the simple dissociation theory; they do not, however, require that it should be discarded. The work here referred to brings out the importance of another factor in the mechanism of electrolytic dissociation, namely, *the chemical contrast of solute and solvent. In other words, the solvent is never really a neutral medium.* In the ordinary equations of the electrolytic theory, however, *e.g.* in the simple deduction of Ostwald's Dilution Law, we consider the solute alone. It is evident from the above that we must also take into account the chemical nature of the solvent. How this general modification of the dissociation theory is to be carried out remains to be seen. At the present stage, however, it does not seem wise to discard the theory *in* *toto* as is done by Kahlenberg and others, solely on the ground of discrepancies—many of which (as in the case of Walker's explanation of amphoteric electrolytes) may be found on further examination to be actually explicable on the basis of the theory. There is hope, indeed, that the most striking anomaly with which the theory of electrolytic dissociation has to deal, namely, the behaviour of strong electrolytes, may after all be brought into line. As a further instance of the application of the theory of electrolytic dissociation to cases in which a definite *rôle* is assigned to the solvent, the reader is referred to the work of Bagster and Steele (*Trans. Faraday Soc.*, **8**, 51, 1912) upon electrolysis in liquefied sulphur dioxide.

We have considered in some detail the theory of electrolytic dissociation in its application to homogeneous equilibria[1] in liquid solutions. Further applications will be made later in discussing heterogeneous equilibria (*e.g.* solubility relations, the "solubility product" and its bearing upon chemical analytical methods, etc.) and chemical kinetics. It will also be necessary to return to the theory from the standpoint of thermodynamics. It may be well at this juncture, however, to refer the reader to a critical survey of the theory by Noyes, in an address at the St. Louis Exhibition, 1904, and later an address by G. N. Lewis before the American Chemical Society (also published in the *Zeitsch. physik. Chem.*, **70**, 212, 1910), entitled "The use and abuse of the ionic theory".

---

[1] An important field of investigation, namely, the so-called neutral salt action, will be discussed later (Chap. IX.). A definite catalytic effect is now attributed to the undissociated molecule as well as to the ion.

CHAPTER VI.

Chemical equilibrium in homogeneous systems (*continued*)—Solid solutions.

SOLID SOLUTIONS.

RELATIVELY little is known about the state of solid solution or the conditions of equilibrium which exist therein. It will be evident, too, from what follows, that the methods of investigation really deal with conditions which belong rather to heterogeneous equilibria (as, of course, strictly do all determinations already mentioned, of vapour pressure, lowering of freezing-point, or rise of boiling-point); and these will be taken up later as examples of such equilibria. In the first place, we must distinguish between crystalline solid solutions or mixed crystals and amorphous solid solutions, such as the mixtures of silicates constituting glasses. These latter have no definite melting-point, but pass by a process of gradual softening into the mobile liquid state. They are therefore looked upon as liquids—supercooled liquids—of very high viscosity. The fact that they are supercooled, and therefore unstable, is shown by the gradual transformation into the crystalline or true solid form, this being the process involved in the devitrification of glass. Since the change from the visibly liquid to the amorphous state is a gradual one, there is no reason for putting any limit to the applicability of the laws of solution to the amorphous "solid" state. The only difference is that the progress towards equilibrium in such a case must be extremely slow owing to the enormous viscosity.

We are at present, however, dealing with the true crystalline solid state. The first question is—does the solute in such a case lower the vapour pressure of the solvent? In this connection von Hauer and Lehmann noticed that hydrated salts—a particular case being lead sulphite—which tend to effloresce, thereby indicating a high vapour pressure, effloresced to a less extent when some other sulphite, such as $CaSO_3$ or $SrSO_3$, was present. Such *homogeneous* mixtures can be made by freezing out a solution containing both. The same effect was noted in the case of the mixture of iron alum and aluminium alum. The decrease in efflorescence shows the lowering of vapour pressure due to the solute, and hence the solution shows a behaviour analogous to liquid solutions.

Other work to which reference might be made is that of Speranski (*Zeitsch. physik. Chem.*, **46**, 70, 1903; *ib.*, **51**, 45, 1905), who measured the vapour pressures of solid solutions of p-dichlorobenzene with p-dibromobenzene, and of p-chlorobromobenzene with p-dibromobenzene. He concluded that "the regular laws which hold for liquid solutions also hold for solid solutions". Perman and Davies (*Trans. Chem. Soc.*, **91**, 1114, 1907) have investigated the vapour pressures of naphthalene and dilute solid solutions of naphthalene with β-naphthol; and more recently the system camphor-borneol has been investigated in a similar manner by E. Vanstone (*Trans. Chem. Soc.*, **97**, 429, 1910). Some of the results obtained by Vanstone may be quoted here by way of illustration. The vapour pressures of camphor and borneol were determined separately by two methods—one a static method by direct readings of the barometric column; and secondly a dynamic method by drawing air across the substance, and analysing the final composition of the gas. The following results were obtained :—

CAMPHOR VAPOUR PRESSURE IN MILLIMETRES OF MERCURY.

Temp. ° C.	Vapour Pressure (Barometric Method).	Temp. ° C.	Vapour Pressure (Air Current Method).
78·6	7·09 mm.	78·1	6·83 mm.
96·8	16·15 „	95·1	15·88 „
111·0	33·00 „	110·9	33·00 „
131·0	75·00 „	131·1	75·20 „
157·0	181·5 „	156·0	185·4 „

The agreement between the two methods is satisfactory.

BORNEOL VAPOUR PRESSURE.

Temp. ° C.	Vapour Pressure (Barometric Method).	Temp. ° C.	Vapour Pressure (Air Current Method).
77·9	2·16 mm.	78·0	2·30 mm.
96·8	6·55 „	95·2	6·67 „
110·0	15·00 „	110·5	15·70 „
131·9	40·92 „	130·2	40·4 „
156·0	115·16 „	150·2	96·6 „
—	—	158·4	127·2 „

Solid solutions were then made simply by fusing the two substances in the required proportions—both solids are completely miscible. The following data refer to 110° C. :—

Mols. Borneol per 100 Mols. Mixture.	Vapour Pressure of Solid Solution Determined by Air Current Method. (The Barometer Method Results agree fairly well with these.)
10	30·52 30·62 30·12
20	27·81 27·90
30	27·10 27·26
40	25·21 24·86
50	24·00 23·96
60	20·87 20·88
70	19·93 19·94
80	18·24 18·17
90	17·90 17·81
100	15·00 15·10
	· (duplicate measurements)

If we consider camphor as the solvent—it having the higher vapour pressure—it will be seen that the addition of the borneol causes a lowering of the vapour pressure somewhat in the same way as dissolved sugar lowers the vapour pressure of water. The case is, however, much more analogous to a mixture say of alcohol and water, for both constituents have measurable vapour pressures whose order of magnitude is much the same. In the ordinary simple cryoscopic expressions for determining the molecular weights of solutes, one of the main assumptions is that the solute shall be non-volatile compared to the solvent. When the solute is volatile an expression for its effect on the vapour pressure of the solvent, as well as upon the freezing-point and boiling-point, can be obtained on thermodynamical grounds. This is evidently analogous to the case we are dealing with in the camphor-borneol system. Such systems as these, however, are much more conveniently considered under the section dealing with phase equilibria especially from the standpoint of the Phase Rule, to which important generalisation we shall come later.

A general conclusion which has been reached in connection with solid solutions is that the molecules of the solute are *not* polymerised more than in the liquid solution state, though one might have expected otherwise. Thus let us take the case of the mixed crystals of thallium nitrate and potassium nitrate investigated by Fock, *Zeit. Kryst. Min.*, **28**, 337 (1897).

The potassium nitrate was present in the *aqueous* solution in large amount and at constant concentration. To this was added thallous nitrate in increasing quantities, the homogeneous solid mixed crystals of both salts which separated from the solution being analysed. The large amount of KNO_3 in the liquid solution threw back the dissociation of the $TlNO_3$, so that we are dealing mainly with undissociated molecules. Some of the results obtained at 25° are as follows:—

Concentration of $TlNO_3(c_1)$ in the Liquid Solution.	Concentration of KNO_3 in the Liquid.	$TlNO_3$ Molecular per Cent.[1] in the Solid $= (x_1)$.	$\frac{c_1}{x_1}$.
0·3238	3·2658	2·77	0·117
0·1869	3·2944	1·78	0·105
0·0663	3·2981	0·57	0·116
0·0231	3·2851	0·20	0·116
0·0089	3·2515	0·08	0·111

From the above it will be seen that the concentration of the $TlNO_3$ in the mixed crystal is proportional to its concentration in aqueous solution. Now, from considerations in connection with the Distribution Law, to which frequent reference will be made later in connection with heterogeneous equilibria, it can be shown that when the ratio of the concentrations of a given substance distributed between two phases is constant, *i.e.* independent of the absolute amount dissolved in the phases, then the substance which is undergoing distribution must have the same molecular weight in the two phases. Since we know that the molecules of $TlNO_3$ are simple in the aqueous solution they must also be simple in the mixed crystal.

---

[1] Molecular per cent. = number of gram-molecules of $TlNO_3$ in 100 gram-molecules of the mixture.

We can also take a few examples from the crystalline mixtures exhibited by some non-electrolytes. Thus, take the case of iodine and benzene.[1]

On freezing out a part of a solution of benzene which contains iodine, the pure benzene does not separate out alone, but always admixed with some iodine. The connection between the concentration of iodine in the liquid benzene and that in the solid is as follows :—

Liquid Solution Concentration of Iodine.	Solid Solution Concentration of Iodine.	Ratio $\frac{[\text{Iodine}]\text{ in Solid}}{[\text{Iodine}]\text{ in Liquid}}$
3·39 per cent.	1·279 per cent.	0·377
2·587 "	0·925 "	0·358
0·945 "	0·317 "	0·336
		Mean 0·357

Since the ratio is approximately constant, for reasons just given it follows that the molecular weight of iodine is the same in liquid as in solid benzene. Since it is known in liquid benzene to have the molecular weight corresponding to I_2, it must also exist in the solid mixed crystal as I_2. Exactly similar relations are found in the case of benzene and thiophene, *i.e.* the latter is C_4H_4S both in liquid benzene and in solid benzene.

In certain cases we may even find that in the mixed crystal one of the components has a smaller molecular weight than in the ordinary case. Thus take the case of hydrogen gas and palladium. These are supposed to form a compound, a hydride which mixes homogeneously with the metal. [Details of this particular instance will be taken up in discussing heterogeneous equilibria, as there are certain peculiarities which call for remark.]

The following data show the connection between the concentration of the hydrogen in the gaseous form and that in the metal in contact with the gas :—

(P) Pressure of H_2 Gas (a Measure of its Concentration in the Gaseous Phase).	Volume of Pd in c.c. (v) which Contains 2 mg. of Hydrogen.	Pv.	$v\sqrt{P}$.
26·2	3·084	80·8	15·8
82·8	1·827	151·3	16·6
165·4	1·299	214·8	16·6
393·7	0·771	303·5	15·3

---

[1] Van 't Hoff's Lectures, II. 75.

It will be seen that the concentration of hydrogen in the gas phase (measured by P) is not proportional to the concentration of gas in solid phase $\left(\text{measured by } \frac{1}{v}\right)$, but that the square root of the concentration of the gas in the gas phase is proportional to the concentration of the gas in the solid phase. From consideration of the Distribution Law (a generalisation to be discussed under heterogeneous equilibria), the above behaviour can be explained by assuming that the hydrogen in the palladium exists as atomic hydrogen, H, not H_2.

The above instances quoted give a general idea of our knowledge of the chemistry of the solid state. It is evidently scanty. Reactions between solutes in the ordinary sense of the term, involving the final arrival at an equilibrium point, have not yet been investigated. The slowness with which reactions can proceed in most cases renders investigation impracticable. It must be clearly borne in mind that in the above cases of solid solution or mixed crystals, we are speaking of homogeneous mixed crystals. Of course, heterogeneous masses of crystals are common, but these are not "mixed" in the true sense. It can evidently happen that a homogeneous state of mixed crystals can give rise to a heterogeneous mixture on altering some condition, such as temperature or concentration. We have frequent examples of this in metallic alloys. Thus, if we prepare some HgCd alloys (by heating the metals together), and allow the alloy to reach the ordinary temperature, it will in general solidify (provided enough Cd is present). If we do not exceed about 10 per cent. Cd, the resulting alloy is a homogeneous solid. If we exceed this amount of Cd, the solid generally disintegrates into a heterogeneous mixture with crystals of different type lying side by side. Or, again, if we start with pure molten iron and add a small quantity of carbon, we find the melting-point of the iron lowered. We also find on analysis that the solid at a given temperature in equilibrium with the molten solution contains some carbon, though at a smaller concentration than in the liquid state. This lowering of melting-point of the metal continues on further addition of the carbon up to the solubility limit of C in Fe. The solid which has separated out at various temperatures corresponding to a given carbon content is homogeneous—a homogeneous solid solution—but if this be allowed to cool down it becomes heterogeneous, giving rise to a solid having a different structure and different properties. This final state is not a solid solution.

A striking experimental test which can be applied to solid solutions is the following. Some of the powdered solid is placed inside a Geissler tube, which is evacuated and current passed through the tube, the cathode discharge being in active operation. Under these conditions the solid solution will fluoresce. No explanation has been offered of this remarkable phenomenon, though the phenomenon itself has been employed as a test of the degree of purity of certain rare earth preparations at the various stages of the separation—since usually a number of the rare earths are found together, presumably in a state of solid solution mainly.

For further information upon solid solutions the reader is referred to the monograph "Solid Solutions," by G. Bruni (*Ahrens Sammlung*, **6**, 1901), also Desch's *Metallography* (Sir William Ramsay's Textbooks of Physical Chemistry).

CHAPTER VII.

Chemical equilibrium in heterogeneous systems from the kinetic standpoint, effects due to capillarity, radiation, etc., being absent—Nernst's Distribution Law—Gas-liquid systems—Liquid-liquid systems—Solid-liquid systems—Gas-solid systems—Solid-solid systems—Solubility and the "solubility product".

GENERAL CONSIDERATION OF HETEROGENEOUS EQUILIBRIA.

A HETEROGENEOUS system is one which consists of more than one physical state or *phase*, and the equilibrium of the phases and of the components amongst the different phases is termed heterogeneous equilibrium. Thus liquid water in contact with water vapour in an enclosed space at a given temperature is an instance of heterogeneous equilibrium. In this case if the temperature be kept constant, the pressure of the system, *i.e.* the vapour pressure, remains constant, as also does the amount of each phase for infinite time. Typical heterogeneous equilibria occur in the following cases:—

Gas in contact with liquid
Gas ,, ,, solid
Liquid ,, ,, liquid
Liquid ,, ,, solid
Solid ,, ,, solid

No heterogeneous equilibrium can exist between gas and gas, since all gases are completely miscible.

Heterogeneous equilibria are governed by two principles or generalisations: first that known as the DISTRIBUTION LAW, and secondly that known as the PHASE RULE. The latter is independent of any molecular theory being deduced from the principles of thermodynamics in which energy changes (as opposed to molecular changes) accompanying any process are considered. The Phase Rule may be regarded as a comprehensive generalisation, which is rather qualitative than quantitative—in the sense that the law of mass action is quantitative.[1] In a sense it may be said to include the Distribution Law, though not explicitly. Let us consider these two principles briefly.

We are already familiar with the concept of a statistical equilibrium between molecules in a *homogeneous* system. Now in the case of liquid water in contact with saturated water vapour we may likewise consider that the equilibrium is statistical, being reached when the number of molecules passing from the liquid to the vapour in a given time is equal to the number passing in the opposite direction. The molecules of water may be said to distribute themselves between the two phases, the equilibrium being governed by a principle analogous to that of the Distribution Law. In the analogous case of a gas distributing itself between a solvent (water, say) and the space above the solvent, a statistical equilibrium with respect to the molecules of the gas is also set up. If the quantity of gas in the gas phase be doubled, then (in the simplest case) the quantity dissolved must also be doubled in order that the number of gas molecules passing from the gas phase to the solution per second shall be equal to the number passing in the opposite direction. Now doubling the quantity of gas in the gas phase at constant volume means doubling the gas pressure. This has caused the concentration of gas in the water to be doubled. In other words, the concentration of dissolved gas is proportional to the gas pressure. This is HENRY'S LAW (1803), which is thus seen to be a particular case of the Distribution Law. Now consider a somewhat different case—one in which a chemical reaction in the ordinary sense may take place in one of the phases (say the gaseous phase), and simultaneously a molecular distribution takes effect between the two phases. An example of this type of heterogeneous equilibrium is afforded by the partial dissociation of ammonium chloride vapour in contact with the solid. The reaction in the vapour phase is—

---

[1] It would be better, perhaps, to say that the law of mass action involves a term, the "constant," characterised by a certain *numerical* value. The Phase Rule contains no analogous term.

$$\underset{\text{Undissociated.}}{NH_4Cl} \rightleftarrows \underset{\text{Gas.}}{NH_3 + HCl}$$

and the law of mass action applied to the homogeneous gaseous phase requires that—

$$\frac{C_{NH_3} \times C_{HCl}}{C_{NH_4Cl}} = \text{constant (at a given temperature).}$$

The equilibrium expression assumes the existence of some undissociated NH_4Cl molecules in the gaseous phase, and the effect of the presence of the solid NH_4Cl is to cause the gas space to be saturated with respect to undissociated NH_4Cl molecules, and thus to cause the concentration of the undissociated gas molecules to remain constant (at constant temperature), so that the mass action expression becomes—

$$C_{NH_3} \times C_{HCl} = \text{constant.}$$

Such a reaction is always spoken of as a heterogeneous one, and the name is convenient. More strictly, however, the "chemical" reaction itself is a homogeneous one, modified by a distribution law effect in the case of one of the reacting substances of such a nature that the concentration of this substance is constant at constant temperature.

The concept of statistical molecular equilibrium does not cover, however, all the phenomena connected with heterogeneous equilibrium, co-existence of phases, and continuity of state. Let us consider the case of liquid water in equilibrium with water vapour. We know that there is a wide range of temperature throughout which these two phases can co-exist, the vapour pressure altering continuously with the temperature. There is, however, a temperature limit (the critical temperature) beyond which such a type of equilibrium cannot exist. Thus we may raise the temperature of the liquid water-vapour system from 0° C. to 365° C., and find a continuous series of equilibrium states, the equilibrium pressure rising finally to a very high value (200 atmospheres). Above the critical temperature, however, heterogeneous equilibrium is impossible, and the homogeneous equilibrium which sets in is that of the spatial distribution of the molecules taken account of by the gas laws and equations of state. Again, if we consider the same system at low temperatures we find that at 0° C. (under atmospheric pressure) water in the *solid* form begins to separate out, and we thus obtain three phases: solid, liquid, and gaseous. At one single temperature, namely, 0·008° above zero, and under the pressure of the saturated vapour, we find these three phases co-existing in equilibrium. On slightly lowering the temperature, the liquid phase disappears, *i.e.* becomes solid, the system now consisting of solid and vapour between which over a wide temperature range (as far as we can measure it in fact) on the lower side of 0° C. we again find a continuous series of statistical equilibria set up. The statistical principle will not account for the *complete* transformation (disappearance) of a phase except as a possibility. Neither will it account for the fact that liquid, solid, and gaseous H_2O can only exist in equilibrium at a single temperature and pressure. This remarkable fact can, however, be anticipated on the basis of the principle known as the Phase Rule, which, as already mentioned, is based upon thermodynamical considerations. The Phase Rule predicts also that liquid water and vapour can co-exist in equilibrium over a temperature range, and similarly for ice and vapour and ice and liquid. It will not predict, however, that a critical point would be reached.

In addition to the equilibrium between a liquid and its saturated vapour, heterogeneous equilibrium is also set up between a solid and its saturated solution, or in the distribution of a substance such as picric acid between two immiscible solvents such as benzene and water in contact. This latter case is a typical instance of an equilibrium governed by the Distribution Law. In *any* case of heterogeneous equilibrium, the Phase Rule and Distribution Law are simultaneously operative; it is only for the sake of clearness that we consider them apart.

The first complete statement of the Distribution Law was made by Nernst (*Zeitsch. physik. Chem.*, **8**, 110, 1891). The following description is taken largely from the introduction to Nernst's paper.[1]

---

[1] As regards the *principle* of distribution, reference should be made to a paper by P. Aulich (*Zeitsch. physik. Chem.*, **8**, 105, 1891), who stated the principle independently of Nernst some years previously (1887), though it is to the latter that we owe the real introduction of the idea into chemistry.

THE DISTRIBUTION LAW.

If a substance possesses the same molecular weight in the gaseous and in the dissolved state, its partial pressure in the vapour, which is in equilibrium with the solution, is proportional to its concentration in the latter (*i.e.* the solution). Nernst calls this the law of van 't Hoff.

If a dissolved substance distributes itself between two different liquids which are only slightly miscible (*e.g.* iodine shaken up with water and carbon disulphide), the above law at once leads to a second, namely, that in the equilibrium state at a given temperature the *ratio* of the concentration of the dissolved substance in each solvent is independent of its absolute mass, or, in other words, the dissolved substance possesses a constant distribution coefficient when it possesses the same molecular weight in both solvents.

If several gases are present simultaneously in the same solvent, or several dissolved substances distribute themselves simultaneously between two given immiscible solvents, there is no effect upon the concentration ratio of any *one* of them (due to the presence of the others) presupposing the absence of any chemical interaction between molecules of different kind. That each single gas in a mixture of gases is absorbed in proportion to its own partial pressure was pointed out by Dalton; that mixtures of dissolved substances which do not react with one another, distribute themselves as though each were alone present in the system, has been shown by Berthelot (*Ann. Chim. et de Phys.* [4], **26**, 417, 1872) to be a completely analogous phenomenon to the Dalton Absorption Law. One can unite both the foregoing expressions into one, namely, at a given temperature for each molecular species there exists a constant distribution ratio between two solvents or between one solvent and the vapour space in contact with it, no matter whether other molecular species are present or not.

The important extension which Nernst gave to the above principle is the following: The above law holds good (when correctly applied) even when a chemical reaction does take place between the different molecular species. For example, if we consider a substance which has undergone partial electrolytic dissociation in one of the solvents, existing thus as undissociated molecules and ions, then each species may still possess a constant distribution ratio (characteristic of itself). The principle is best understood by an example. Consider the distribution of succinic acid between water and ether. The acid is not dissociated at all in ether; the molecular weight is normal. In water it undergoes slight electrolytic dissociation. Nernst's idea is that a constant ratio is found for the concentration of the undissociated part of the acid in the water and the (total) acid in the ether, and this ratio is independent of the total mass of succinic acid in the heterogeneous system as a whole. The ions are not soluble in ether, and therefore for each of them the distribution ratio, if one can use the term, is also constant, being either 0 or ∞.

A slightly more complex state of affairs is met with in the case of benzoic acid in certain solvents, *e.g.* benzene, in which a partial polymerisation of the acid occurs according to the equation

$$2C_6H_5COOH \rightleftarrows (C_6H_5COOH)_2.$$

In water the same acid is not polymerised, but suffers a very slight electrolytic dissociation. If water and benzene are brought into contact, and benzoic acid allowed to distribute itself between the two, Nernst's principle states that for the simple non-dissociated unpolymerised molecules of acid present in each phase a certain distribution ratio holds good independent of the total mass of benzoic acid in the system as a whole. Neither the polymerised molecules nor the ions can be said to possess a distribution coefficient, it being either 0 or ∞.

GAS-LIQUID SYSTEMS.

The modification of Henry's Law when the molecular state of the gas in the gas phase differs from that in the solution.

In obtaining the simple expression of proportionality between gas pressure and concentration of dissolved gas, it was assumed that the gas on dissolving underwent no chemical change (polymerisation or dissociation). Henry's Law is to be modified when such effects are present.

Let us suppose the dissolved gas is partly polymerised. If we denote simple gas molecules by X and the polymerised molecules by X_2, the reaction equilibrium we are considering in solution is

$$2X \rightleftarrows X_2.$$

Applying the law of mass action we obtain at a given temperature

$$C_{x_2} = KC_x^2 \text{ or } C_x = \sqrt{\frac{C_{x_2}}{K}}.$$

Now Nernst's extension of the van 't Hoff Law of Distribution states that direct proportionality exists between the concentration of like molecules in the two phases, or what is the same thing, there is direct proportionality between the gas pressure P (which is due entirely to simple X molecules) and the concentration C_x of the simple dissolved molecules. If we denote this proportionality factor by K′ we can write the above statement in the form

$$P = K'C_x.$$

Now substituting the value $\sqrt{\frac{C_{x_2}}{K}}$ for C_x in this expression, we obtain—

$$P = K'\sqrt{\frac{C_{x_2}}{K}}$$

and since $\frac{K'}{\sqrt{K}}$ is a constant, say K_2, we obtain finally—

$$P = K_2\sqrt{C_{x_2}}$$

Now if practically all the dissolved gas molecules exist in the polymerised form X_2 the term C_{X_2} will very nearly represent the *total concentration of the dissolved gas*, so that in this particular case the concentration of the dissolved gas will be proportional to the *square* of the pressure of the undissolved gas. If the degree of polymerisation had been higher than 2, say *n*, so that the dissolved molecules of gas were represented by X_n, and if, further, practically all the gas dissolved were in this condition, then the concentration of the dissolved gas would be proportional to the *n*th power of the gas pressure. In the case of dissociation of X into smaller individuals the value of *n* would be less than unity, but the same distribution principle will hold good.

It is important to observe that union of the *solvent* with simple gas molecules X will not in any way alter the applicability of the simple Henry-van 't Hoff Law. Thus suppose the solvent is water, and further suppose that some of the dissolved gas molecules are hydrated, the reaction, which is in equilibrium in solution, is

$$X + H_2O \rightleftarrows XH_2O.$$

The law of mass action applied to this yields the relation

$$\frac{C_X \times C_{H_2O}}{C_{XH_2O}} = K.$$

But if the solution is dilute the concentration of the solvent C_{H_2O} is constant, and we can therefore write—

$$\frac{C_X}{C_{XH_2O}} = K_1.$$

Now the distribution equilibrium of the simple X molecules gives us the relation—

$$P = K'C_X$$

and combining this with the above we obtain

$$P = K'K_1C_{XH_2O}$$

where P is the gas pressure. Writing $K'K_1$ as K_2 we get—

$$P = K_2C_{XH_2O}.$$

That is, the concentration of the hydrated molecules is proportional to the gas pressure, just as is the concentration of the unhydrated gas molecules. To state the Henry-van 't Hoff Law correctly we must therefore say:—

Direct proportionality exists between the gas pressure of a partly dissolved gas and the concentration of the dissolved gas when the latter exists either in the form of simple gas molecules or as hydrated gas molecules, the solution being a dilute one.

In the general case it will be evident that distribution experiments will give us useful information respecting the molecular state of dissolved substances.

LIQUID-LIQUID SYSTEMS.

Consider a substance distributed between two immiscible solvents. If chemical action is absent (polymerisation, dissociation), the distribution law takes the simple form—

$$\frac{C_I}{C_{II}} = \text{constant}$$

where C_I is the concentration of the solute in solvent I.
and C_{II} „ „ „ „ solvent II.

These concentration terms refer to the total solute present in a given volume of each phase. This was verified by Berthelot and Jungfleisch for the case of the distribution of bromine and iodine between water and carbon disulphide. The ratio remained constant even when the absolute values of the concentration terms varied from 1 to 10. Both elements possess normal molecular weights (Br_2, I_2) in each solvent. When any chemical effect enters, such as polymerisation or dissociation, the distribution law expression—

$$\frac{C_I}{C_{II}} = \text{constant}$$

only holds for certain parts of the dissolved substance present in each phase, *e.g.* for the normal benzoic acid molecules in the case mentioned previously of the distribution of this acid. By applying the law of mass action, however, to the equilibria conditions which are set up in one of the phases when distribution equilibrium has already been attained, it is possible to transform the distribution law expression into a shape which is in certain cases more amenable to experimental verification. Let us take a case in which polymerisation of solute may occur to form double molecules in both solvents in contact, though to quite different amounts. In the first solvent suppose the double molecules are present to a small extent, their concentration being x, and $(c_1 - x)$ the concentration of the normal molecules in the same solvent. Then the reaction—

$$(AB)_2 \rightleftarrows 2AB$$

when one applies the law of mass action to the case of the first solvent, yields the relation—

$$\frac{(c_1 - x)^2}{x} = K_1$$

where K_1 is the equilibrium constant of the reaction in the first solvent. Similarly, if we denote the simple molecules in the second solvent by y, and double molecules by $c_2 - y$, we obtain—

$$\frac{(c_2 - y)}{y^2} = K_2.$$

According to the distribution law for the simple molecules one obtains—

$$\frac{c_1 - x}{y} = \text{constant} = k_1$$

and for the double molecules—

$$\frac{x}{c_2 - y} = \text{constant} = k_2.$$

Hence $$\frac{(c_1 - x)\sqrt{K_2}}{\sqrt{c_2 - y}} = k_1 \text{ or } \frac{(c_1 - x)^2}{c_2 - y} = k_0.$$

If now we are dealing with the case in which benzene is in contact with water, and an organic acid such as benzoic is distributed between the two, we know that on the benzene side the concentration of simple molecules (y) can be neglected compared to that of the double molecules, and similarly on the water side the double molecules x can be neglected compared to the single molecules; and further, if we neglect the electrolytic dissociation, which is very small for the majority of organic acids, we find that the distribution law becomes—

$$\frac{c_1^2}{c_2} = k_0$$

where c_1 = the concentration of the undissociated normal benzoic acid molecules in the water (*i.e.* practically the entire solute present in the water);

c_2 = the concentration of the "double-moleculed" acid in the benzene, *i.e.* practically all the acid present.

The experimental verification of such conclusions as the above was undertaken by Nernst, notably in the case of acetic acid and phenol, which, according to freezing-point molecular weight determinations, are each normal in water, but very largely polymerised to double molecules in benzene (when the concentration is sufficiently large).

The Distribution of Acetic Acid between Benzene and Water.—Nernst made use of the Beckmann freezing-point method. 5·075 grams water were placed in the tube, and 31·5 grams benzene above it. The freezing point of the mixture, *i.e.* the freezing point of the benzene, was determined. Owing to the exceedingly small solubility of the water in benzene, the freezing point was practically that of pure benzene, namely, 5·9° C. On adding successive quantities of acetic acid, which distributed itself between both solvents, the corresponding lowering of the freezing point of the benzene layer was determined. This lowering corresponded to the quantity of acetic acid dissolved in the benzene; in order to determine this concentration term separate experiments were carried out with known quantities of acetic acid dissolved in moist benzene, and the corresponding freezing points noted. The results are given in the following table, in which t represents the observed lowering of freezing point; c_2 the number of grams of acetic acid in benzene corresponding to t, and obtained by means of the separate experiments; c_1 the number of grams of acetic acid which were present in the 5·075 grams water (obtained by subtracting c_2 from the total amount used).

t.	c_2.	c_1.	$\frac{c_1}{c_2}$.	$\frac{c_1^2}{c_2}$.
0·075°	0·043	0·245	5·7	1·40
0·120°	0·071	0·314	4·4	1·39
0·158°	0·094	0·375	4·0	1·49
0·240°	0·149	0·500	3·4	1·67

It will be noted that $\frac{c_1}{c_2}$ is much less constant than $\frac{c_1^2}{c_2}$; since the latter increases with increasing concentration, we can infer that while acetic acid in benzene exists mainly in the form of double molecules at small concentrations, the number of single molecules cannot be neglected. Analogous results were obtained for the distribution of phenol between water and benzene, as well as the distribution of benzoic and salicylic acids between the same solvents. For details Nernst's paper should be consulted. A further account of distribution experiments and data will be found in an article by Herz in *Ahrens Sammlung*, vol. **15**, 1910.

Determination of Hydrolysis (of Salts) by Distribution Measurements.—The principle of the method will be made clear by considering a specific case, namely, the hydrolysis of aniline hydrochloride. Suppose one mole of this salt dissolved in a certain volume v of water, and further suppose the degree of hydrolysis is x, then the concentration of the free aniline is $\frac{x}{v}$ gram-molecules per liter. If now a layer of benzene of known volume be poured upon the water, the aniline will distribute itself between the two layers. The quantity of aniline present in the benzene can be estimated by analysis. Separate experiments with aniline itself distributed between water and benzene are carried out and the distribution ratio determined. Knowing this ratio and the quantity of aniline actually present in the benzene layer above the aqueous solution of aniline hydrochloride, it is easy to determine the concentration of the aniline in the aqueous layer, and hence obtain x, the degree of hydrolysis. It is assumed that the quantity of aniline removed into the benzene layer is negligible compared with the quantity represented by x.

The Process of Extraction.—According to the distribution law, for a substance the molecular weight of which is identical in two immiscible solvents, the relationship holds good—

$$\frac{c_{\mathrm{I}}}{c_{\mathrm{II}}} = \text{a constant dependent only upon temperature.}$$

Let us suppose the concentration to go on increasing by successive addition of solute until the solubility s of the solute is reached in one phase, say in I. Then the distribution law says—

$$\frac{s_{\mathrm{I}}}{c_{\mathrm{II}}} = \text{constant.}$$

But at a given temperature s is a constant, and therefore c_{II} must be a constant independent of the further quantity of solute added to the system; no further solution can take place in solvent I., and the distribution law makes c_{II} also constant, and hence c_{II} at this point must likewise be the limiting concentration, or the solubility of the solute in solvent II. Hence the distribution law may be put in the form: the distribution of the solute at any concentration up to saturation takes place in the ratio of the solubilities of the solute in the phases.

Now, if we have an aqueous solution of an organic substance, and wish to extract the solute with a limited quantity of benzene (say), the question is, What is the most advantageous way to use the benzene? Should it be added all at once, or in successive small quantities? The best results as far as extraction is concerned are obtained by the second method. This will be seen from the following considerations. Suppose that the substance is twice as soluble in benzene as it is in water. The distribution law constant is therefore 2. If the amount of the substance in 1 liter of water is A, and we add the whole of the benzene, say 1 liter, we shall have $\frac{A}{3}$ remaining in the water, and $\frac{2}{3}$A in the benzene—this latter being the quantity extracted. Now suppose we employ the benzene in two equal stages. That is, to 1 liter of aqueous solution we add $\frac{1}{2}$ liter of benzene. Let x be the amount extracted. Then A − x remains in the water, and—

$$\frac{\frac{x}{\frac{1}{2}\text{ (liter)}}}{\frac{A - x}{1\text{ (liter)}}} \text{ must still be equal to } 2$$

that is

$$x = \frac{A}{2}.$$

By using $\frac{1}{2}$ liter benzene we have extracted half the solute leaving half behind. On adding a fresh $\frac{1}{2}$ litre of benzene to the aqueous layer, we extract half of what remains of the solute; that is to say, $\frac{1}{4}$A, so that both operations have resulted together in the extraction of $\frac{3}{4}$A. In the previous case, with the same quantity of benzene, $\frac{2}{3}$A was extracted. Hence the second process is the more advantageous. Theoretically an infinite number of extractions with infinitely small quantities of benzene would be the most advantageous method; but in practice considerations of time naturally come in.

Further Applications of the Distribution Law.—Nernst concludes his paper with certain considerations, to some of which reference will now be made. If one alters the extent of (electrolytic) dissociation of a volatile electrolyte in a liquid phase, then its vapour pressure (the partial pressure due to the solute) will be altered, as would also be its concentration in a second solvent if such be in contact. Thus the partial pressure of hydrochloric acid over its aqueous solution will *increase*, for example, when one adds to the solution a second electrolyte with a common ion (*e.g.* NaCl), and will *decrease* when the latter does not possess a common ion, since the vapour (HCl) consists of undissociated molecules in equilibrium with the undissociated molecules present in the solution. Again, salicylic acid in dilute aqueous solution would pass over in large quantity into a benzene layer in contact when a strong acid or a salt of salicylic acid is dissolved in the aqueous layer. The addition of the latter causes some of the salicylic ions (C_6H_4OHCOO') to unite with the $H^{\cdot}$ ions to form a number of undissociated molecules of acid, and since there must be a constant distribution ratio for these undissociated molecules between the two solvents, it follows that their concentration in the benzene layer must increase also; that is, some further salicylic acid passes from the aqueous into the benzene layer.

Consider now a general case of a solution containing a number of substances which are volatile, and let a chemical reaction between the solutes take place as follows—

$$n_1A_1 + n_2A_2 + \ldots = n'_1A'_1 + n'_2A'_2 + \ldots$$

Suppose equilibrium is established when the partial pressures of the different species are $p_1p_2 \ldots p'_1p'_2 \ldots$, and their concentration terms are $c_1c_2 \ldots c'_1c'_2 \ldots$ Then applying the law of mass action to the two phases—solution and vapour—we obtain—

$$\frac{p_1^{n_1}p_2^{n_2}\ldots}{p'^{n'_1}_1 p'^{n'_2}_2 \ldots} = \mathrm{K} \text{ (for the vapour phase)}$$

$$\frac{c_1^{n_1}c_2^{n_2}\ldots}{c'^{n'_1}_1 c'^{n'_2}_2 \ldots} = \mathrm{K}' \text{ (for the liquid phase).}$$

The distribution law gives a number of equations of the type—

$$c_1 = k_1p_1 \qquad c_2 = k_2p_2 \qquad c'_1 = k'_1p'_1 \qquad c'_2 = k'_2p_2$$

where k_1, k_2, k'_1, k'_2 are the solubility coefficients for each molecular species, which are a function of temperature alone. From the above we get finally by division—

$$\mathrm{K} = \mathrm{K}'\frac{k'^{n'_1}_1 k'^{n'_2}_2}{k_1^{n_1}k_2^{n_2}}.$$

This result is of considerable importance. In most cases it is possible to determine the solubility of a given molecular species in a solvent, and by means of the above relation it is possible to foretell how a number of substances will react in a given solvent, if the kind and extent of the reaction in the gaseous state is known, and *vice versâ.* The same conclusion holds good if we are dealing with the distribution relations of a series of substances between two solvents. The above general theorem has been investigated by Kuriloff (*Zeitsch. physik. Chem.*, **25**, 419, 1898).

GAS-SOLID SYSTEMS.

The simplest type of gas-solid heterogeneous equilibrium is furnished by the phenomenon of sublimation, which is exactly analogous to the process of vaporisation, and just as in this latter case the equilibrium corresponds to the setting up of a constant vapour pressure at any given temperature, the pressure being independent of the mass or volume of the system provided some solid still remains as such.

Another type which may also be regarded as belonging to a similar category is the vapour-solid equilibrium of salts containing water of crystallisation, *e.g.* $CuSO_45H_2O$. The vapour consists of H_2O molecules, and at a given temperature there is a constant pressure, as one would expect, since the active mass of the solid[1] is constant.

The classic example of a gas-solid equilibrium which involves a distinct chemical reaction, is the dissociation of $CaCO_3$ into lime and CO_2—

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

At any given fairly high temperature there is a definite equilibrium established, the existence of which is shown by the constancy of the CO_2 pressure. That this constancy is to be expected may be shown as follows.

In the gas phase there are some undissociated $CaCO_3$ molecules, some CaO molecules, and a very large number of CO_2 molecules. The reaction stated applies to this phase. The law of mass action therefore leads to the relation—

$$\frac{C_{CaO} \times C_{CO_2}}{C_{CaCO_3}} = \text{a constant at constant temperature.}$$

But the presence of *solid* $CaCO_3$ and CaO, as we have already seen, means that the active mass, *i.e.* the concentration or partial pressure, of each of these is constant, and therefore the above expression becomes C_{CO_2} = constant at constant temperature, or p_{CO_2} = constant. This has been found to be the case. The following are a few of Le Chatelier's[2] values for p_{CO_2} in the above system given for the sake of showing the magnitude of the equilibrium pressure of CO_2 at various temperatures.

$t°$ C.	547°.	740°.	810°.	865°.
p_{CO_2} in mm. of mercury	27	255	678	1333

On adding CO_2 to the above system at constant volume the "degree of dissociation" will be thrown back just as in homogeneous systems, *i.e.* some $CaCO_3$ will be formed, and since the system is saturated with respect to this it will separate out as a solid. Of course, if CO_2 *at* the equilibrium pressure be brought into contact with the $CaCO_3$—CaO—CO_2 system by simply making connection to another vessel containing the CO_2 gas, there will be no chemical effect produced in the system. Further, if one brings CO_2 at *less* than the equilibrium dissociation pressure into contact with *lime* alone *no* carbonate will be formed. The addition of solid $CaCO_3$ or CaO to the equilibrium system $CaCO_3$—CaO—CO_2 will not have any chemical effect, since the active mass of the solid is independent of its total mass, and no further CO_2, for example, is produced by adding some more solid carbonate or lime. (Of course, if one had started with a small quantity of carbonate in a large space and raised the system to an exceedingly high temperature, the dissociation might go on until no more *solid* $CaCO_3$ were left, though there would always be some $CaCO_3$ gaseous molecules in existence, since dissociation is never absolutely complete although it may be made practically so. In such a case the active mass of the $CaCO_3$ is no longer constant—there being no solid—and introduction of some solid will cause a further dissociation to take place, *i.e.* more CO_2 will be formed until the equilibrium is again established. As long, however, as any solid $CaCO_3$ is present the same CO_2 pressure will manifest itself at a given temperature.)

---

[1] The solid is heterogeneous, consisting of two salts, in the above case the penta- and trihydrate

[2] Le Chatelier (*Compt. Rend.*, 102, 1243, 1886).

Now consider another familiar case—the dissociation of solid ammonium hydrosulphide. It is supposed to take place according to the reaction—

$$\underset{\text{Solid.}}{NH_4HS} \rightleftarrows \underset{\text{Gas.}}{NH_3} + \underset{\text{Gas.}}{H_2S}.$$

If this is so, then on applying the law of mass action we get—

$$\frac{p_{NH_3} \times p_{H_2S}}{p_{NH_4HS}} = \text{a constant,}$$

or, since p_{NH_4HS} is constant as long as there is solid in the system, it follows that—

$$p_{NH_3} \times p_{H_2S} = \text{a constant.}$$

This has been experimentally proved by Isambert (*Compt. Rend.*, **92**, 919, 1881; **93**, 731, 1881; **94**, 958, 1882), by adding some NH_3 or H_2S to the system and noting the final equilibrium state reached (at a given temperature).

$p_{(NH_3)}$.	$p_{(H_2S)}$.	$p_{NH_3} \times p_{H_2S}$.
208 mm.	294 mm.	61,152
138 "	450 "	63,204
417 "	146 "	60,882
452 "	143 "	64,779

When no excess of either component had been added the *total* pressure P was observed to be 501 mm. at 25·1°. Since equimolecular quantities of each gas are produced, it follows that one half of the observed pressure, namely, 250·5 mm., is due to each gas. That is—

$$p_{NH_3} \times p_{H_2S} = \frac{P^2}{4} = (250{\cdot}5)^2 = 62{,}750,$$

which agrees well with the above constant.

On adding excess solid NH_4HS to the system which already contains some solid in equilibrium with the gases, no effect is produced for the reasons already given in the analogous case of $CaCO_3$. On adding NH_3 or H_2S the dissociation is thrown back, and since each of these enters into the equation to the same degree it is immaterial which we add. Some undissociated NH_4HS is formed which comes out as solid. As long as the temperature is constant, however, the equilibrium constant is the same, that is $p_{NH_3} \times p_{H_2S}$ = constant, as Isambert's experiments show. Of course the actual concentration (or partial pressure) of the gaseous components NH_3 or H_2S is altered by the addition of *one* of them, as necessarily follows in order that their product may be constant, but while the product is constant the total pressure is in this case not constant. On adding some H_2S (say) the total pressure increases, although ($p_{NH_3} \times p_{H_2S}$) remained constant. Now what is the effect of compressing the system at constant temperature?

If solid NH_4HS is present the effect is nil. Some NH_3 and H_2S unite to form some solid NH_4HS, leaving at all stages of the compression the value ($p_{NH_3} \times p_{H_2S}$) constant, and since $p_{NH_3} = p_{H_2S}$ the total pressure is likewise constant. If the temperature and volume of the system are such that no solid NH_4HS is present, we can no longer regard p_{NH_4HS} as constant, but must consider the whole expression—

$$\frac{p_{NH_3} \times p_{HS}}{p_{NH_4HS}} = \text{constant.}$$

If such a homogeneous system be compressed at constant temperature a certain amount of NH_4HS will be formed, that is, the partial pressures of all these components will increase in such a way as to make the above expression constant. Neither the total pressure nor the product $p_{HN_3} \times p_{H_2S}$ is in this case constant until we reach the point at which solid NH_4HS is formed, from which stage the product $p_{NH_3} \times p_{H_2S}$ is constant, and since there is not excess of any component the total pressure must be likewise constant on further diminishing the volume.

Another example, which has the historical interest of having been the first case of dissociation of solids to which Horstmann, in 1877, applied the law of mass action, is the decomposition of solid ammonium carbamate—

$$NH_2COONH_4 \rightleftarrows 2NH_3 + CO_2.$$

The dissociation is very nearly complete at moderate temperatures, that is $p_{NH_2COONH_4}$ is small compared to p_{NH_3} and p_{CO_2}.

The law of mass action gives the relation—

$$\frac{p^2_{NH_3} \times p_{CO_2}}{p_{NH_2COONH_4}} = \text{a constant at constant temperature.}$$

As long as solid carbamate exists in the system its partial pressure is constant, that is

$$p^2_{NH_3} \times p_{CO_2} = \text{constant.}$$

When no excess of either gas has been introduced it is evident that, if P is the total pressure, the NH_3 pressure is $\frac{2}{3}P$ and that of CO_2 is $\frac{P}{3}$, since there are twice as many NH_3 molecules produced as CO_2 molecules. The equilibrium expression, therefore, may be put in the form—

$$\frac{4P^2}{9} \times \frac{P}{3} = \frac{4P^3}{27} = \text{constant.}$$

(If excess of either gas be added the ratios of the partial pressures are no longer 2 : 1; but in any case as long as solid is present

$$p^2_{NH_3} \times p_{CO_2} \text{ is constant.)}$$

It will be seen that this case differs from the NH_4HS case, since one of the gaseous components is raised to a higher power than the other. Addition of NH_3 in this case has, therefore, a greater effect in throwing back the dissociation than has addition of CO_2.

When the system is such that no solid carbamate is present the relations are more striking. We have already considered it as an instance of homogeneous equilibrium. It was shown, p. 153, that under certain conditions addition of NH_3 has no effect on the extent of dissociation, while CO_2 *causes* dissociation.

The next instance of dissociation of a vapour which we shall consider is that of ammonium chloride. The dissociation reaction is

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

This is one of those dissociations which only take place when a trace of moisture is present. It was shown by Baker (*Trans. Chem. Soc.*, **65**, 615, 1894) that when great precautions are taken to exclude moisture the vapour of ammonium chloride consists entirely of undissociated molecules, the molecular weight corresponding to the formula NH_4Cl. When, however, a little moisture is present, as in the case in the "ordinary" methods of drying the substance, dissociation according to the above equation takes place. Baker found that at a temperature of 350° C., employing the Dumas bulb method, the degree of dissociation appeared to be almost complete. A similar result was obtained by other investigators employing the Victor Meyer method as well as that of Dumas, so that it came to be recognised as a fact that ammonium chloride vapour—except when dried with exceedingly great care—existed in the state of practically complete dissociation. This was the position when Smith and Lombard (*J. Amer. Chem. Soc.*, **37**, 39, 1915) took up the problem of the vapour density of the substance and succeeded in showing that this generally accepted statement was by no means correct when applied to the truly *saturated* vapour. Their method consisted in filling bulbs, previously evacuated, with the saturated vapour and determining the density from weight and volume measurements. The following is a brief résumé of Smith and Lombard's investigation. In the first place Smith and Lombard point out the extremely important fact that in all previous density determinations the *unsaturated* vapour only has been investigated. Now experiment shows that in the region of 357° C. the dissociation pressure of ammonium chloride vapour is about 1150 mm., so that employing the open bulb Dumas method—the bulb being open to the atmosphere to allow of expulsion of the air—the vapour finally dealt with must be very far from saturation and therefore dissociation is favoured. The fact therefore that values indicating 91-100 per cent. dissociation are thus obtained does not prove that the vapour when saturated is dissociated to this extent. As regards the use of the Victor Meyer method it is pointed out that dissociation must have been promoted by diffusion of the vapour into the air inside the tube, and that therefore any value for the dissociation up to complete dissociation might be expected from this method. Smith and Lombard point out that "the fact that the facile Victor Meyer method is applicable indeed to the *detection* of the existence of dissociation (if this has not been detected otherwise already), but is valueless for the study of the *extent* of such dissociation, seems to have been too generally overlooked". The method employed by them is free from the sources of error—as regards the true magnitude of dissociation of the saturated vapour—already pointed out. In Smith and Lombard's experiments the ammonium chloride recrystallised was kept in a desiccator over phosphorus pentoxide. The substance was therefore dry in the ordinary sense, but not so excessively dry as to prevent dissociation. The vapour density was determined at 10° intervals from 280° to 330°, the first temperature being that at which the density becomes large enough to be accurately measured, and the second that at which the dissociation pressure becomes nearly equal to the atmospheric pressure. (The experimental arrangement employed did not permit of determinations beyond this.) The data obtained are given in the following table. The final results are accurate to ± 2 – 3 per cent. The saturated vapour pressures quoted are those of Smith and Calvert (*Journ. Amer. Chem. Soc.*, **36**, 1373, 1914). The densities δ_m which the vapour would have if it were *un*dissociated (expressed in moles per liter) and yet gave the measured dissociation pressure are calculated by the formula

$$\delta_m = \frac{1}{22 \cdot 4} \cdot \frac{273}{T} \cdot \frac{P}{760}.$$

In the column headed "completely dissociated" are the densities which the vapour would have if it were wholly dissociated. These values are just one half of the δ_m values.

DENSITIES OF AMMONIUM CHLORIDE VAPOUR (SATURATED).

Temperature in degrees Centigrade.	Vapour Density				Observed Pressure (total) in mm. of Mercury.
	Observed		Calculated		
	Grams per c.c.	Moles per liter Δ_m.	Undissociated (moles per liter) δ_m.	Completely Dissociated moles per liter.	
280	0·000135	0·00252	0·00392	0·00196	135·0
290	0·000169	0·00316	0·00528	0·00264	185·3
300	0·000230	0·00430	0·00707	0·00354	252·5
310	0·000307	0·00573	0·00939	0·00470	341·3
320	0·000406	0·00759	0·01239	0·00620	458·1
330	0·000531	0·00993	0·01624	0·00812	610·6

From these data one can calculate the degree of dissociation by applying the formula—

$$\alpha = \frac{\delta_m - \Delta_m}{\Delta_m}$$

where α is the degree of dissociation. The results are as follows :—

DEGREE OF DISSOCIATION OF SATURATED NH_4Cl VAPOUR.

Temperature °C.	Percentage Observed.	Dissociation Smoothed Value.
280	(55·5)	66·8
290	67·1	66·0
300	64·2	65·2
310	63·8	64·4
320	63·3	63·6
330	63·6	62·8

These results show conclusively that *saturated* ammonium chloride vapour does not exceed 67 per cent. dissociation. Ammonium bromide, also investigated by Smith and Lombard, shows considerably less dissociation.

"The fact that the vapour density [of ammonium chloride vapour] increases and that the degree of dissociation *diminishes* with rising temperature, is at first sight anomalous. It must be remembered, however, that the results are not obtained with constant total pressure (as in the Dumas and V. Meyer methods), but with rapidly rising total pressure (vapour pressure). Thus between 290° C. and 330° C. the partial pressure of free ammonia or HCl (as will be shown in a later table) rises from 73·7 mm. to 234·5 mm., while the total pressure increases from 185·3 mm. to 610·6 mm., or almost in the same proportion. If we calculate the change in partial pressure of free ammonia which would occur between the same limits of temperature if the total pressure were kept constantly at 185·3 mm., we find that this partial pressure would rise from 73·7 to 83·6 mm. Thus at a constant pressure of 185·3 mm. the density would diminish and the degree of dissociation would *increase* from 66 per cent. to 82 per cent."

We now pass on to calculate the dissociation constants for the saturated vapour at various temperatures. The dissociation constant K_c is given by the equation

$$K_c = \frac{a^2}{1 - a} \Delta_{mi}.$$

The symbol Δ_{mi} denotes interpolated or smoothed values for the observed vapour density. Δ_{mi} is calculated by the formula

$$\Delta_{mi} = \frac{\delta}{1 + a_{\text{interpolated}}}$$

and is simply the density which the saturated vapour would have if it gave the interpolated values of a instead of the measured values. In the following table two sets of values for K_c are given. The first set denoted by the term "observed" is calculated from the directly observed values of the density Δ_m and the a values obtained therefrom. The second set denoted by the term "average" is calculated from the smoothed values of a and the quantity Δ_{mi}. The "average" values for K_c are presumably the more reliable since experimental error has been eliminated to a certain extent.

DISSOCIATION CONSTANTS OF SATURATED NH_4Cl VAPOUR.

Temperature °C.	K_c Observed.	K_c Average.
280	0·00174	0·00316
290	0·00432	0·00407
300	0·00496	0·00523
310	0·00644	0·00665
320	0·00828	0·00842
330	0·0110	0·0106

Further, with the aid of the density data obtained we can calculate the partial pressures of ammonium chloride and of ammonia (or of HCl) in the saturated vapour at various temperatures.

The expressions are—

$$p_{\text{NH}_4\text{Cl}} = \text{P}_{\text{total}} \times \frac{2\Delta_{mi} - \delta_m}{\delta_m}$$

and

$$p_{\text{NH}_3} = p_{\text{HCl}} = \frac{\text{P}_{\text{total}} - p_{\text{NH}_4\text{Cl}}}{2}.$$

The following table contains the data of Smith and Lombard:—

PARTIAL PRESSURES IN SATURATED AMMONIUM CHLORIDE VAPOUR.

Temperature °C.	P_{total} in mm.	p_{NH_4Cl} (Undissociated Molecules) in mm.	$p_{NH_3} = p_{HCl}$ in mm.
280	135·0	30·3	52·4
290	185·3	37·9	73·7
300	252·5	53·2	99·7
310	341·3	73·8	133·8
320	458·1	101·2	178·5
330	610·6	141·7	234·5

We have discussed ammonium chloride vapour in considerable detail. There remains, however, one point more, known as the anomaly of ammonium chloride vapour. It has already been mentioned that Baker discovered that very dry ammonium chloride gave rise to vapour completely undissociated, that is consisting of NH_4Cl molecules only. The difference between ordinarily dry solid NH_4Cl and excessively dry NH_4Cl is at first sight so small that one would expect both sorts to possess the same active mass and therefore give rise to the same value for the saturated vapour pressure due to the *undissociated* molecules. In the case of the absolutely dry substance the vapour pressure is entirely due to undissociated molecules. In the case of the ordinary dry substance the vapour consists partly of NH_3 and HCl molecules as well. We would expect, however, that in the latter case the partial pressure of the undissociated molecules (p_{NH_4Cl}) should be identical with the total pressure observed in the case of the absolutely dry substance, for according to Dalton's Law of mixed gases each constituent exerts its own pressure value independent of the other gases present. The vapour pressure of the absolutely dry (undissociated) substance has been measured by F. M. G. Johnson (*Zeitsch. physik. Chem.*, **61**, 458, 1908) with the following results:—

Temperature °C.	Vapour Pressure P in mm.
256	57
284	156
332	540

If the values be compared with the values for the partial pressure of the undissociated NH_4Cl molecule obtained by Smith and Lombard, it will be seen at once that the vapour pressure over the specially dried material is much greater than the partial pressure of NH_4Cl over the partially dissociated substance. In fact Johnson's values are in rough agreement with the *total* pressure as measured by Smith and Lombard. This stands in direct contradiction to the deduction based on mass action. That this discrepancy exists was first pointed out by Abegg. Considerable discussion has taken place as to its possible cause (*cf.* Annual Reports of the Chemical Soc., V., 1908, pp. 24, 25). Wegscheider's view that solid ammonium chloride can exist in two allotropic modifications, according as to whether moisture is present or not, seems to fit the facts best, though it appears at the same time to be somewhat artificial. It has been found by Scheffer, as a matter of fact (*Proc. Akad. Wetensch.*, Amsterdam, **18**, 446, 1915) that two allotropic forms of ammonium chloride exist, the transition temperature being 184·5° C. Scheffer, however, doubts if this is really in agreement with Wegscheider's hypothesis (*Proc. Akad. Wetensch.*, Amsterdam, **18**, 1498; 1916). The problem therefore remains unsolved.

An interesting example of "double decomposition" occurs in the action of steam on iron according to the equation

$$\underset{\text{Solid.}}{3Fe} + \underset{\text{Gas.}}{4H_2O} \rightleftarrows \underset{\text{Solid.}}{Fe_3O_4} + \underset{\text{Gas.}}{4H_2}$$

The equilibrium equation is—

$$\frac{p_{Fe_3O_4} \times p^4_{H_2}}{p^3_{Fe} \times p^4_{H_2O}} = \text{a constant at constant temperature.}$$

Since Fe_3O_4 and Fe are solids, and therefore constant as regards their active mass, the equation reduces to

$$\frac{p^4_{H_2}}{p^4_{H_2O}} = \text{constant, or } \frac{p_{H_2}}{p_{H_2O}} = \text{constant.}$$

This is borne out by the following results:—

Temp.	p_{H_2}.	p_{H_2O}.	$\frac{p_{H_2}}{p_{H_2O}}$
200	4·6	95·9	0·048
200	9·7	195·3	0·049
440	4·6	25·8	0·178
440	10·1	57·9	0·174

Excess of one or other of the products is added in order to investigate the validity of the theoretical expression.

At about 1500° C. the ratio $\frac{p_{H_2}}{p_{H_2O}}$ is unity, and hence, if H_2 and H_2O vapour at the same partial pressure be passed over Fe or Fe_3O_4, no chemical change takes place.

Other instances of gas-solid equilibria will be discussed later from the standpoint of the affinity relations involved (Vol. II., Chap. XII.).

SOLID-SOLID SYSTEMS.

The equilibria met with in heterogeneous systems containing solids only are known as phase equilibria, analogous to the equilibrium between ice and liquid water, and are taken account of in the Phase Rule, which will be discussed later. Owing to the existence of solids the active masses of all the substances present are constant, so that the idea of a mass action equilibrium being brought about has no longer its usual significance. Such systems are characterised by possessing one or more transition points or temperatures at which the various solids are in equilibrium, but above or below which one phase *completely* disappears. This is quite different from a shift in the equilibrium point or a shift in the equilibrium constant, with temperature such as occurs in gaseous mixtures or solutions. (In solid solutions, however, reactions both homogeneous and heterogeneous can proceed, though so exceedingly slowly at ordinary temperatures that it is impossible to follow them, as can be done, for example, in the case of liquid solutions.) At the transition point referred to above with immiscible solids, the equilibrium is not a mass action equilibrium, since the equilibrium point is unaltered on addition of any of the substances present. Solid-solid equilibria are essentially instances of phase equilibria and will be considered from the standpoint of the Phase Rule.

SOLID-LIQUID SYSTEMS.

The simplest type of equilibrium in such systems—analogous to vaporisation and sublimation—is that of the solubility of a solid in a liquid. From the kinetic standpoint equilibrium is reached when the number of molecules passing from the solid into the solution in a given time is equal to the number passing in the opposite sense. The equilibrium might be regarded as a distributional one in which the active mass of the solid is a constant, and hence its limiting concentration or *solubility* must have a certain value in a certain solvent at constant temperature.

As we have employed the saturated vapour pressure of a substance as a measure of the active mass of the substance, so we can likewise employ its solubility for the same purpose.

Let us consider one or two examples. To start with, we can take the reaction in which a very soluble substance (NaI) reacts with a sparingly soluble substance ($PbSO_4$), represented by the stoicheiometric equation—

$$PbSO_4 + 2NaI = PbI_2 + Na_2SO_4$$

(*cf.* Findlay, *Zeitsch. physik. Chem.*, **34**, 409, 1900).

Lead sulphate and lead iodide are only sparingly soluble in water, and since their concentrations must be, therefore, very small, we assume in accordance with the theory of electrolytic dissociation that the dissociation of the small quantity in solution is practically complete. In the reaction in which we start with $PbSO_4$ and NaI we know that some (insoluble) PbI_2 is formed together with an equivalent quantity of Na_2SO_4. Let us suppose that the sodium salts are also nearly completely dissociated at the concentrations at which they occur. The reaction might be represented thus :—

$$PbSO_4 \text{ (solid)} + 2I' \rightarrow PbI_2 \text{ (solid)} + SO_4''.$$

The presence of the $Na^{\cdot}$ may be left out of account, for it occurs to the same extent on both sides of the equation, since we are assuming that such alkali salts are largely and equally dissociated at the same order of dilution. This, of course, has only a bearing upon the problem if the equilibrium point finally reached corresponds to the point where the concentrations of both alkali salts are nearly equal. Such happens to be the case in this reaction. The above equation, however, might be slightly misleading in the sense that in the actual mechanism of the process we do not suppose that I' acts directly upon the solid $PbSO_4$, but instead comes into contact with the saturated solution of the $PbSO_4$, which we have already considered as being completely dissociated into $Pb^{\cdot\cdot}$ and SO_4''.

As a consequence of the reaction some solid $PbSO_4$ disappears and gives rise to some solid PbI_2. This means that some NaI has been transformed into Na_2SO_4. In other words, some I' has disappeared from solution and SO_4'' has taken its place. From the expression

$$\underset{\substack{\text{(Solid, active mass}\\ \text{is constant.)}}}{PbSO_4} + 2I' \rightleftarrows \underset{\substack{\text{(Solid; active mass}\\ \text{is constant.)}}}{PbI_2} + SO_4''$$

the equilibrium equation should require that

$$\frac{[I']^2}{[SO_4'']} = \text{constant}$$

no matter what may be the original composition of the initial mixture. To test the applicability of the law of mass action we might, therefore, start with solutions of different concentrations of the sodium salts, together with excess of both the sparingly soluble salts, and on allowing equilibrium to be set up the resulting ratio $\frac{[I']^2}{[SO_4'']}$ determined analytically, should be the same in all cases. The results are as follows :—

Initial Concentration of I' (identical with Initial Concentration of NaI) in Gram Equivalents per Litre.	Initial Concentration of SO_4''.	Final (Equilibrium) Concentration in Gram Equivalents per Litre.		$\frac{[NaI]^2}{[Na_2SO_4]}$.
		NaI.	Na_2SO_4.	
0·07084	0·03257	0·06869	0·03470	0·2720
0·06540	0·03784	0·06869	0·03455	0·2732
0·04286	0·00998	0·04158	0·01127	0·3068
0·04010	0·01296	0·04151	0·01154	0·2984
0·02430	0·00222	0·02288	0·00364	0·2871
0·02004	0·00945	0·02520	0·00428	0·2966

The fact that the final values are approximately independent of the initial conditions is evidence that a true equilibrium point is reached.

On the view that the degree of ionisation of a salt varies with the dilution, it would be necessary to allow for such an effect in the ratio given in the final column of the preceding table. It would now appear, however, in view of recent work of a thermodynamic character, that such a mode of correction is scarcely legitimate. The newer ideas regarding the behaviour of salts will be found in Volume II. in the chapter dealing with the activity theory of solutions. Incidentally it should be mentioned that Findlay substantiated the general correctness of the results quoted above by electromotive force measurements. This can not be understood until the reader is acquainted with the theory of electromotive force given in Volume II.

It is possible on the basis of considerations dealt with in the next section, namely the concept of the solubility product or ionic product, to find independent confirmation of the results quoted above. Anticipating familiarity on the part of the reader with the term ionic product, it can be stated that for lead sulphate the ionic product, $L = [Pb^{\cdot\cdot}][SO_4'']$ = $1 \cdot 2 \times 10^{-8}$ at 25° C., and similarly for lead iodide at the same temperature $L = 4 \cdot 3 \times 10^{-9}$. Consequently the ratio

$$\frac{[I']^2}{[SO_4'']} = 0 \cdot 36$$

which agrees roughly with the value obtained by Findlay.

In the reaction just considered it will be noted that owing to the slight solubility of $PbSO_4$ and PbI_2, we can neglect the quantity of SO_4'' ion or I' produced by these compared with the concentration of these ions produced by the alkali salts. Hence the justification of simplifying the mass action expression down to the ratio $\frac{[I']^2}{[SO_4'']}$ derived practically entirely from the alkali salts, as a sufficient criterion of the equilibrium point of the whole reaction.

We may also look at the same reaction from a slightly different standpoint.

Suppose we start with a solution containing only NaI and Na_2SO_4. Further, let us suppose that there is too much I' present to give the value of the ratio $\frac{[I']^2}{[SO_4'']}$ which it possesses when the $PbSO_4$, NaI, system is in equilibrium. Let us add a small quantity of a soluble lead salt. PbI_2 alone will be formed and precipitated in order to bring down the ratio $\frac{[I']^2}{[SO_4'']}$ towards the value indicated.

Similarly, if there had been too much SO_4'', we would have had pure $PbSO_4$ precipitated in order to make the ratio approach the equilibrium value. Suppose that—in either case—the addition of a soluble lead salt is continued until the $\frac{[I']^2}{[SO_4'']}$ has attained the equilibrium value—a process which will involve the precipitation of one single salt or the other—then at this point, on adding further soluble lead salt, both PbI_2 and $PbSO_4$ will begin to come down in equivalent proportions, always keeping the ionic ratio $[I']^2/[SO_4'']$ constant. It will be noted, therefore, that it is not necessarily the most insoluble salt which is precipitated first as was formerly supposed. Which salt is precipitated depends on the relative concentration values of the ions which determine the equilibrium. We might represent the behaviour diagrammatically—see Fig. 49.

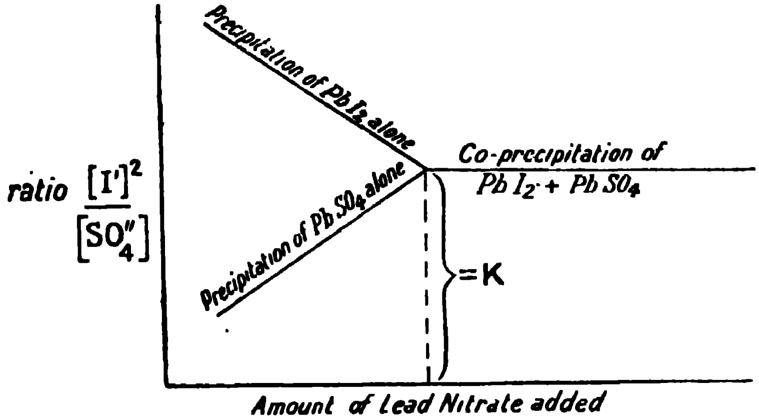


FIG. 49.

The Solubility Product or Ionic Product (*Elementary Treatment*).—For the introduction of this important conception into heterogeneous electrolytic equilibrium we are indebted to Nernst (*Zeitsch. physik. Chem.*, 4, 372, 1889). We are familiar with the application of the law of mass action in the form of Ostwald's dilution law to the electrolytic dissociation of water itself, namely—

$$H_2O \rightleftarrows H^{\cdot} + OH'$$

the equation taking the form—

$$\frac{C_{H^{\cdot}} \times C_{OH'}}{C_{H_2O}} \quad \text{constant,}$$

or, since the concentration of the water is constant, $C_{H^{\cdot}} \times C_{OH'} =$ constant. This constant may be called the "ionic product" as well as ionisation constant. In the case of saturated solutions of electrolytes in which some solid is present, the idea of distribution, as we have seen, would lead to an equilibrium being set up when there is equality in the number of molecules passing in opposite directions to and from the solid. The ratio of the concentration in the two phases is constant at the equilibrium point by definition, and since the "concentration" in the solid is constant, the concentration of molecules in solution is constant as long as we can regard the solvent as the same, *i.e.* as long as it is unmodified by the presence of the ions themselves. It will be noted that we are dealing with the distribution of the same kind of molecular species as is necessary in accordance with Nernst's definition of the distribution law.

Now let us consider the application of the law of mass action to the dissolved state, *i.e.* the ions and molecules. If we are dealing with a simple binary dissociation such as that of AgCl into $Ag^{\cdot}$ and Cl', we have the relation—

$$\frac{[Ag^{\cdot}][Cl']}{[AgCl]} = \text{constant}$$

supposing the simple form of the law of mass action, *i.e.* the dilution law, to hold good. But we have just seen that in the saturated state [AgCl] is constant—

$$\therefore [Ag^{\cdot}][Cl'] = \text{a constant}$$

called the SOLUBILITY PRODUCT OR IONIC PRODUCT. This is of fundamental importance in dealing with solubility relations of electrolytes especially of sparingly soluble salts. It will be seen from the above that if we increase the concentration of either ion, the other ion will decrease in concentration in order to keep the concentration product constant. Thus if we add KCl to AgCl saturated, the $Ag^{\cdot}$ must decrease in concentration. It can only do so by forming some undissociated AgCl. But the solution is saturated, and in accordance with the distribution or partition law, the concentration of AgCl (undissociated) is constant, and hence some of the undissociated AgCl is precipitated in the solid form. The total solubility of AgCl is therefore less in presence of KCl than it is in pure water. At the same time it is important to note that the concentration (solubility) of the undissociated molecules is the same whether KCl is present or not, provided KCl is not in such quantity as to alter the nature of the solvent. It is evidently in accordance with the idea of the active mass of the solid being constant no matter what substances may be introduced into the liquid in contact with it. The conclusion that the dissolved undissociated molecules possess a constant concentration having a certain numerical value, holds, of course, only as long as we keep to the same solvent. It might be possible to add so much extraneous material, *e.g.* alcohol, say, to an aqueous solution of saturated AgCl, as to alter the concentration of the dissolved undissociated AgCl molecules. This would appear to be in contradiction to the idea of the solid AgCl having a constant active mass. It must be remembered, however, that a proportionality, and not an identity exists between the active mass of a solid, and the concentration of undissociated dissolved molecules. The proportionality further varies with the *nature* of the solvent, but is independent of the chemical nature of the solid, which is partially dissolved.[1] (This, of course, assumes that no specific chemical action comes in between solid and solvent, as in the case of Na in contact with water.) In the cases here considered the dissociation is supposed so great that we only take ions into consideration. To return to the case of the saturated aqueous solution of silver chloride. In the presence of KCl or other electrolyte having an ion in common with one or other of the ions of the sparingly soluble body, its solubility is said to be decreased. This statement is true if we are referring to the concentration of the ion, which has *not* been increased by addition of a soluble electrolyte (KCl). In pure water AgCl dissolves slightly, giving rise to a quantity of $Ag^{\cdot}$ and Cl', which are evidently present in equivalent amounts. The solution might be looked upon as symmetrical with respect to the ions. The ionic product has a certain value, L_0. On adding KCl, some solid AgCl is precipitated. The Cl' is increased, the $Ag^{\cdot}$ is correspondingly decreased in such a way as to make $[Ag^{\cdot}][Cl'] = L_0$, as before. The solution is now asymmetric with respect to the $Ag^{\cdot}$ and Cl'. In speaking of solubility in such a case we fix our attention on the amount of Ag and Cl in equivalent proportions, which still remain in the solution, and could be withdrawn from it. That is, we fix our attention on the ion least represented. In the case of AgCl in presence of KCl, the $Ag^{\cdot}$ ion is evidently the ion least represented. The solubility of a sparingly soluble electrolyte in presence of soluble electrolyte with a common ion is evidently a more composite term than the solubility of an electrolyte (or non-electrolyte) in the solvent alone. Again, as already pointed out, the saturated solution of a body such as AgCl is very dilute, and since it is a salt, the small quantity which is dissolved suffers almost complete dissociation in solution. Hence the concentration of the undissociated molecules must be small compared even to that of the ions. That is, C_0 is negligible compared to the concentration $[Ag^{\cdot}]$ or $[Cl']$. Hence in such a case, say, when AgCl is dissolved in water alone, the concentration of $Ag^{\cdot}$ OR of Cl' in gram ions per liter gives a number identical with the solubility of the entire salt. But $[Ag^{\cdot}] \times [Cl'] = L_0$. Hence the solubility is identical with the $\sqrt{\text{solubility product}}$. Now take the case of AgCl in presence of some KCl. The solubility simply becomes identical with the concentration of the least represented ion, *i.e.* the $Ag^{\cdot}$ ion. An estimation of the $Ag^{\cdot}$ ion in solution is therefore the experimental way of arriving at the solubility of AgCl in aqueous KCl solution. We can evidently calculate this quantity if we know what value L_0 has—say by estimating the $Ag^{\cdot}$ *or* Cl' in *absence* of KCl—and remembering that L_0 is constant whether KCl is present or not. By the addition of the KCl in a given amount we know the quantity of Cl' present (the Cl' originally present from the AgCl itself being usually negligible compared to the quantity thus added), and the "solubility" of the AgCl in presence of KCl, or the $Ag^{\cdot}$ concentration is simply—

---

[1] This, of course, does not mean that all salts have the same solubility in a given solvent, for salts have different active masses.

$$(Ag^{\cdot}) = \frac{L_0}{[Cl']}.$$

More frequently, as a matter of fact, one employs the ionic product to calculate the solubility of a salt such as AgCl in water alone from data obtained when KCl is present. In the latter case an easy method of determining the $Ag^{\cdot}$ ion present in a known quantity of KCl (known Cl' ion concentration) is afforded by electromotive measurements to which we shall come in dealing with the subject of electro-chemistry. Having determined the $Ag^{\cdot}$ concentration in such a case and knowing the Cl' concentration, the product of the two gives the solubility product, L_0. When AgCl is dissolved in water alone we have seen—

assuming practically complete dissociation—that the solubility (which is now symmetrical in respect to each ion) is simply $\sqrt{L_0}$, and hence the solubility may be easily obtained without an actual determination in pure water—an operation of considerable difficulty.

By way of showing that the addition of a common ion to a saturated solution of an electrolyte causes the remaining ion or ions to diminish in concentration in accordance with the expression $\frac{[\text{cation}]\ [\text{anion}]}{[\text{undissociated electrolyte}]} = $ a constant, one may quote the following figures given by Nernst (*Zeitsch. physik. Chem.*, **4**, 379, 1889):—

Solubility of Silver Acetate in gram-molecules per liter. (Aqueous Solution).	Concentration of added Sodium Acetate.
0·0603	0
0·0392	0·061
0·0282	0·119
0·0208	0·230

Solubility of Silver Acetate.	Concentration of Silver Nitrate added.
0·0603	0
0·0417	0·061
0·0341	0·119
0·0195	0·230

The solubility of silver acetate decreases with increasing concentration of either sodium acetate or silver nitrate, and for equivalent amounts of each the solubility is approximately equally reduced.

In the deduction of the principle of the constancy of the ionic product given above, we have postulated the existence of some undissociated dissolved molecules of the salt. In view, however, of the X-ray examination of crystal structures (of which a brief account has already been given in an earlier chapter) which has led to certain conclusions regarding the ionic space lattice upon which at least simple salts are built up, it would seem more logical not to assume the existence of the undissociated molecule at all at any stage in the process of solution. The following alternative treatment is that given by J. A. V. Butler (*Chem. and Ind.*, **43**, 634, 1924).

An ion leaves the surface and passes into solution when it has acquired by thermal agitation sufficient energy to carry it out of the range of the attractive forces at the crystal surface. An ion becomes deposited when it reaches the surface from solution at a place at which it can become permanently attached. In the simplest case of a cubic lattice a positive ion must be deposited above a negative one and *vice versa*, in order to continue the crystal lattice. It follows that the rate at which an ion leaves the surface is proportional in the first place to the number in the surface layer, whilst the rate of deposition of an ion is proportional to its concentration in solution and to the number of places at the surface at which it can become attached. Equilibrium is attained when equal numbers of both kinds of ions are dissolved and deposited in the same time.

Now consider the state of the crystal surface in contact with the solution. Take the case of a crystal normally containing equal numbers of positive and negative ions in its surface layer. In contact with solution there may be a greater tendency for the one ion to leave or to become deposited at the surface than the other.

It is evident that the loss of a positive ion exposes a negative ion and *vice versa.*

Suppose that at equilibrium Nx positive ions and $N(1 - x)$ negative ions are exposed at the surface.

Then we can write the following proportionalities:—

Rate of solution of positive ions $= k_1Nx$,
Rate of deposition of positive ions $= k_2N(1 - x) . C_1$,
Rate of solution of negative ions $= k_3N(1 - x)$,
Rate of deposition of negative ions $= k_4NxC_2$;

where C_1 and C_2 are the concentrations of the positive and negative ions in solution.

For equilibrium $k_1Nx = k_2N(1 - x)C_1$
and $k_3N(1 - x) = k_4NxC_2$
whence $C_1 \times C_2 = \frac{k_1k_3}{k_2k_4} = K$

which is the law of the solubility product.

It is evident that if the addition of electrolytes whether containing a common ion or not causes any change in the conditions of solution (*e.g.* by affecting the attraction of the solvent for the ions) the quantities k_1, k_2, etc., will not remain constant. The fact that the "law" is at best an approximation becomes evident.

PRECIPITATE FORMATION AND THE METHODS OF ANALYTICAL CHEMISTRY.

We are now in a position to understand the conditions which determine the formation or non-formation of a precipitate by the interaction of ions.

A sparingly soluble electrolyte—acid, salt, or base—will be precipitated from solution when the product of the concentrations of the ions present exceeds a certain value, *viz.* the solubility product. The principles are quite the same for the three kinds of electrolytes named, but the most important case for our present purpose is that of the formation of salts which are only slightly soluble in the solvent.

If we bring $AgNO_3$ and KCl together in a solution so dilute that the product $[Ag^{\cdot}] \times [Cl']$ is less than the solubility product L_0 for the given salt (AgCl) in the particular solvent, then no precipitate is formed. This in practice is rare, because L_0 for this salt is extremely small.

What has been said for AgCl holds, of course, equally well for numerous other cases. AgI has a much smaller solubility and therefore much smaller solubility product than AgCl. The question now arises —what is the effect of adding KI solution to some AgCl, and how far will the reaction AgCl + KI = AgI + KCl proceed?

When equilibrium is reached we know that the law of the ionic or solubility product must be satisfied for the saturated solution of each of the bodies AgCl and AgI. That is, the conditions to be satisfied are—

$$\begin{cases} [Ag^{\cdot}] \times [Cl'] = L_{AgCl} \\ [Ag^{\cdot}] \times [I'] = L_{AgI} \end{cases}$$

$$\therefore \frac{[Cl']}{[I']} = \frac{L_{AgCl}}{L_{AgI}} = \text{a constant, K.}$$

That is to say, the reaction goes on until the ratio of the Cl′ : I′ is the same as the ratio of the solubility or ionic products of the sparingly soluble salts. Now according to measurements of Goodwin (*Zeitsch. phys. Chem.*, **13**, 588, 1894),

$$L_{AgCl} = 1{\cdot}56 \times 10^{-10},$$

i.e. the solubility of AgCl in water is $\sqrt{1{\cdot}56 \times 10^{-10}}$,

$$L_{AgI} = 0{\cdot}94 \times 10^{-16}.$$

∴ the ratio is $1{\cdot}6 \times 10^6$. That is to say, the reaction proceeds until the Cl′ concentration becomes over one million times greater than the I′ concentration. *Practically*, therefore, all the AgCl originally present is transformed into AgI.

We may now consider the applicability of the ionic product to Mohr's method of estimating the chlorine content in a soluble chloride by titration with $AgNO_3$, using potassium chromate (K_2CrO_4) as indicator.

For a solution in which the precipitate of silver chromate just permanently appears together with the chloride, we must have—[1]

$$[Ag^{\cdot}][Cl'] = L_{AgCl}$$

$$[Ag^{\cdot}]^2[CrO_4''] = L_{Ag_2CrO_4}$$

$$\text{or } \frac{[Cl']^2}{[CrO_4'']} = \frac{L^2_{AgCl}}{L_{Ag_2CrO_4}} = \frac{(1{\cdot}56 \times 10^{-10})^2}{3{\cdot}34 \times 10^{-12}} = \frac{1}{1{\cdot}4 \times 10^8}.$$

The amount of chromate usually added is one or two drops (0·1 c.c.) of a saturated solution per 100 c.c. of solution, which corresponds to a chromate ion concentration of $2{\cdot}5 \times 10^{-3}$ normal. It follows therefore that, before any silver chromate is permanently precipitated, the concentration of chlorine ion will be reduced to $\sqrt{\frac{2\cdot5 \times 10^{-3}}{1\cdot4 \times 10^{8}}} = 4\cdot2 \times 10^{-6}$, *i.e.* an exceedingly small quantity. That is to say, practically all the chloride originally present (as KCl) has been converted into AgCl, and from the quantity of standard $AgNO_3$ run in it is easy to calculate the chlorine ion originally present.

---

[1] The ionic products (L) are obtained from the observed solubilities of the salts in water in the following way. For silver chloride the solubility (S) in water in moles per litre is equal to $\sqrt{L_{AgCl}}$. For silver chromate the solubility (S) = $\sqrt[3]{\frac{L_{Ag_2CrO_4}}{4}}$. The reason for the numeral 4 in the cube root is as follows. There are twice as many silver ions as chromate ions, *i.e.* $[Ag^{\cdot}] = 2[CrO_4'']$. Hence $[Ag^{\cdot}]^2 = 4[CrO_4'']^2$. Therefore the ionic product $[Ag^{\cdot}]^2[CrO_4'']$ is numerically identical with $4[CrO_4'']^3$. But $S_{Ag_2Cr\;_4} = [CrO_4'']$. Hence $S_{Ag_2CrO_4} = \sqrt[3]{\frac{L_{Ag_2CrO_4}}{4}}$.

A further illustration of similar principles is to be found in the ordinary method of qualitative separation of metals by H_2S in acid and alkaline solution. H_2S is a weak acid, *i.e.* it gives rise to a small number of ions which we can for the moment regard as $H^{\bullet}$ and S''. If we add HCl to the H_2S solution we still further throw back the concentration of S'' ion, for we have increased the $H^{\bullet}$ and we know that $\frac{[H^{\bullet}]^2[S'']}{[H_2S]}$ must be constant. Now it happens to be the case that the sulphides of the metals As, Sb, Sn, Pb, Cu, Hg, Bi, Cd are extremely insoluble, their solubility products being extremely small. These metals may be referred to as 1st Group. On the other hand, the sulphides of the metals of Group II, Ni, Co, Zn, Mn, Fe, are more soluble than those of the 1st Group. If a solution contains metals of both groups and an acidified solution of H_2S is added, the system then contains a very small quantity of S'' ions. In the case of the 1st Group metals, even this small quantity of S'' ions is such that the concentration values of S'' and metal$^{\bullet\bullet}$ exceeds the ionic product of the corresponding metallic sulphide, and hence precipitation of these sulphides takes place. The concentration of S'' is, however, too small to precipitate the 2nd Group metals, for the product of the S'' ions × metal ion$^{\bullet\bullet}$ is less than the solubility product of the sulphides of the 2nd Group. In order to bring down the sulphides of the 2nd Group it is necessary to add a considerable quantity of S'' ions. This is done not by adding the weakly dissociated acid H_2S, but by adding a soluble sulphide, *e.g.* $(NH_4)_2S$, which being a salt is largely dissociated in solution, and hence it is conceivable that the point may be reached when the product of S'' ion and the metal ion of the 2nd Group now exceeds the solubility product of the sulphide and precipitation occurs (It is obvious that $(NH_4)_2S$ will even more completely precipitate the 1st Group metals, but, of course, no separation of Groups I and II could thereby be effected.)

Another important problem frequently met with is the solution of a precipitate by chemical means, *e.g.* the solution of a precipitated sulphide by an acid such as HCl. The process essentially depends on the fact that the precipitate is a salt which contains a weak constituent (anion or cation), and the reagent added must give rise to the complementary ion in large quantity. ZnS suspended in water has a certain solubility and solubility product. On adding $H^{\bullet}$ by means of HCl, it is found that the product of the $[H^{\bullet}]$ and $[S'']$ is of such a magnitude that these ions cannot exist in presence of one another entirely uncombined, and hence some undissociated H_2S is formed, evidently at the expense of the ions. The S'' ion in solution tends to decrease in quantity owing to this recombination, but in order that the solubility product of the ZnS may be maintained constant, further ZnS dissolves in the ionic form. The S''

again rises to too great values, and more undissociated H_2S is formed. In this continuous process the solution is evidently becoming richer in $Zn^{\cdot\cdot}$, richer in undissociated H_2S, and the mass of ZnS precipitate decreases. This can go on until the ZnS is completely dissolved. If we had started with a limited quantity of strong HCl solution, it is clear that the solubility of H_2S in the solution might easily have been exceeded, and since this happens to be a gaseous body it will be evolved as such. It will be observed that the ratio of the values of the solubility product of the metallic sulphide and of the dissociation constant of H_2S is of great importance in determining whether the sulphide will dissolve in a given acid, *i.e.* in presence of a given $H^{\cdot}$ ion concentration or not. Thus take a sulphide such as HgS, which is the most sparingly soluble one known, and add some dilute HCl to a suspension of the sulphide in water. As before we have $H^{\cdot}$ and S'' present together in the solution, but now, owing to the extremely small quantity of S'' present from the sulphide, the product of the $H^{\cdot}$ and S'' is so small that practically there is no union of these to form undissociated H_2S, and hence the metallic sulphide only dissolves to an infinitesimal amount. To get any considerable quantity to dissolve we have to increase the $H^{\cdot}$ as much as possible, and raise the temperature of the system, since the solubility of most solids in liquids increases with a rise of temperature, and even then the solution of the sulphide may not be complete, for evidently the $H^{\cdot}$ becomes used up partially in the process to form undissociated H_2S, and at a certain stage the $H^{\cdot}$ ion may become too low in value to unite further with the S'', *i.e.* to cause further solution of the metallic sulphide. Of course the fact that actually *precipitation* of sulphides of 1st Group metals can take place in moderately acid solution of H_2S shows that in such a case the $H^{\cdot}$ is too small to cause the reverse process, *i.e.* solution of sulphide in presence of the exceedingly small S'', the smallness being due to the small solubility of the metallic sulphide formed. CdS is the most soluble of the 1st Group of sulphides. One would expect, therefore, if we wish to get the precipitate to form, that only a very slightly acid solution is necessary, and that if one used a strong acid solution the S'' present (from the H_2S) would not be great enough to combine with the metal and form the metallic sulphide. It is, therefore, possible to precipitate CdS with H_2S in dilute HCl solution, and to redissolve it by adding more HCl. It is clear from the foregoing consideration that Group II metal sulphides will dissolve much more easily in a solution containing $H^{\cdot}$ ion than will the metal sulphides of Group I—for the solubility and solubility product of Group II metal sulphides is much greater than those of Group I. In general, therefore, every precipitate which is not too insoluble (HgS is near the limit) and which contains a weak anion (*e.g.* carbonates, sulphides, cyanides, phosphates, oxalates, hydroxides) will dissolve in a solution which contains $H^{\cdot}$ ions in sufficient quantity. It is clear from the above that hydroxides should dissolve in presence of $H^{\cdot}$ ion, *i.e.* in acids even more easily than sulphides or carbonates, because the dissociation of the weak "acid" H_2O is less than any other weak acid or base, and hence in the case of an hydroxide, such as $Al(OH)_3$ in suspension in water, the OH' formed from the hydroxide in presence of even a small quantity of $H^{\cdot}$ gives rise to an ionic product which exceeds the ionic product or ionisation product for H_2O, and hence undissociated H_2O is progressively formed, the $Al(OH)_3$ gradually dissolving in order to keep its own solubility product constant.

Hitherto we have regarded the electrolytic dissociation of H_2S as proceeding according to the equation $H_2S \rightleftarrows 2H^{\cdot} + S''$. As a matter of fact, however, it takes place in two stages, each with a definite equilibrium constant, k_1 and k_2, *viz.* $H_2S \rightleftarrows HS' + H^{\cdot}$ and $HS' \rightleftarrows H^{\cdot} + S''$. The whole question of the equilibrium conditions of the metallic sulphides in aqueous solution has been studied by the late Professor Bruner (Bruner and Zawadzki, *Bull. de l'Acad. de Sc. de Cracovie*, July, 1909). A few illustrative examples may be quoted. In general the following relations must be satisfied when the system is in equilibrium—

$$[MeS] = \text{constant}$$

(undissociated dissolved molecules in equilibrium with the solid sulphide)

$$\begin{gathered}
MeS \rightleftarrows Me^{\cdot\cdot} + S'' \\
k[MeS] = [Me^{\cdot\cdot}] \times [S''] \\
H_2S \rightleftarrows H^{\cdot} + HS' \\
HS \rightleftarrows H^{\cdot} + S'' \\
k_1[H_2S] = [H^{\cdot}] \times [HS'] \\
k_2[HS'] = [H^{\cdot}] \times [S'']
\end{gathered}$$

$$\therefore [S''] = k_1k_2\frac{[H_2S]}{[H^{\cdot}]^2}$$

$$\therefore k[MeS] = k_1k_2[Me^{\cdot\cdot}]\frac{[H_2S]}{[H^{\cdot}]^2}$$

$$\therefore \frac{k}{k_1k_2}[MeS] = \frac{[Me^{\cdot\cdot}][H_2S]}{[H^{\cdot}]^2} = K \quad . \quad . \quad . \quad (1)$$

Equation (1) shows that when equilibrium is reached the concentration of the metal ion in the solution is inversely proportional to the concentration of the undissociated H_2S molecules, and directly proportional to the square of the concentration of the $H^{\cdot}$ ion. To test the foregoing conclusions it is necessary to get a case in which a *measurable* equilibrium point exists. Bruner considers zinc salts as unsuitable, owing to the fact that the sulphide precipitation is not a reversible process, but the requisite considerations are met with in the case of thallium.

The equilibrium $2Tl^{\cdot} + H_2S \rightleftarrows Tl_2S + 2H^{\cdot}$ *at* 25° was investigated, first keeping the concentration of the H_2S constant, and secondly allowing it to vary by known amounts. A moderately good equilibrium constant was obtained even when the absolute values of the concentration terms altered over a fairly wide range. This equilibrium constant

K is directly proportional to the solubility product L, as may be seen from equation (1). For metals which give rise to uni-, di-, and trivalent ions respectively, the following relations hold good. For univalent metals—

$$L_1 = [Me^\cdot]^2 \times [S''] \qquad K_1 = \frac{[Me^\cdot]^2 \times [H_2S]}{[H^\cdot]^2}.$$

For divalent metals—

$$L_2 = [Me^{\cdot\cdot}] \times [S''] \qquad K_2 = \frac{[Me^{\cdot\cdot}][H_2S]}{[H^\cdot]^2}.$$

For trivalent metals—

$$L_3 = [Me^{\cdot\cdot\cdot}]^2[S'']^3 \qquad K_3 = \frac{[Me^{\cdot\cdot\cdot}]^2[H_2S]^3}{[H^\cdot]^6}.$$

The sulphur ion concentration is a function of the H_2S and $H^\cdot$ ion concentrations, according to the following:—

$$[S''] = k_1k_2\frac{[H_2S]}{[H^\cdot]^2}.$$

For, according to the law of mass action, we have—

$$k_1[H_2S] = [H^\cdot][HS']$$
$$k_2[HS'] = [H^\cdot][S'']$$

and therefore $$[S''] = k_1k_2\frac{[H_2S]}{[H^\cdot]^2} = k'\frac{[H_2S]}{[H^\cdot]^2}.$$

The first dissociation constant k_1 of H_2S has been determined several times. Auerbach's value is $0\cdot91 \times 10^{-7}$. The second dissociation constant k_2, according to Knox, is $1\cdot2 \times 10^{-15}$. Hence $k' = 1\cdot092 \times 10^{-22}$, and therefore—

$$L_1 = 1\cdot092 \times 10^{-22}K_1$$
$$L_2 = 1\cdot092 \times 10^{-22}K_2$$
$$L_3 = (1\cdot092)^3 \times 10^{-66}K_3.$$

For thallium sulphide $L_1 = 7\cdot0 \times 10^{-23}$ at 25° C.

A few other sulphides are taken from Bruner's table—

MeS.	K.	L.	Concentration of the Metal Ion when $[H^\cdot] = 1(N)$ and $H_2S = 0\cdot1 N$.
MnS . . .	$6\cdot3 \times 10^{6}$	7×10^{-16}	—
FeS . . .	$3\cdot4 \times 10^{3}$	$3\cdot7 \times 10^{-19}$	$3\cdot4 \times 10^{2}$
TlS . . .	$6\cdot37 \times 10^{-1}$	$7\cdot0 \times 10^{-23}$	$2\cdot5$
αZnS . . .	$(7\cdot3 \text{ to } 4\cdot5) \times 10^{-4}$	$(8\cdot0 \text{ to } 5\cdot0) \times 10^{-26}$	$(7\cdot3 \text{ to } 4\cdot5) \times 10^{-3}$
βZnS . . .	*circa* 10^{-2}	$1\cdot1 \times 10^{-24}$	10^{-1}
CdS (from $CdCl_2$)	$6\cdot5 \times 10^{-6}$	$7\cdot1 \times 10^{-28}$	$6\cdot5 \times 10^{-5}$
CdS (from $CdSO_4$)	$4\cdot6 \times 10^{-7}$	$5\cdot1 \times 10^{-29}$	$4\cdot6 \times 10^{-6}$
PbS . . .	$3\cdot1 \times 10^{-6}$	$3\cdot4 \times 10^{-28}$	$3\cdot1 \times 10^{-5}$
CuS . . .	$(5\cdot3 \text{ to } 1\cdot1) \times 10^{-20}$	$(5\cdot9 \text{ to } 1\cdot2) \times 10^{-42}$	$(5\cdot3 \text{ to } 1\cdot1) \times 10^{-19}$
Ag_2S . . .	$(3\cdot6 \text{ to } 1\cdot35) \times 10^{-28}$	$(3\cdot9 \text{ to } 1\cdot47) \times 10^{-50}$	$(6\cdot0 \text{ to } 3\cdot7) \times 10^{-14}$
HgS . . .	$7\cdot9 \times 10^{-26}$	$7\cdot7 \times 10^{-48}$	$7\cdot0 \times 10^{-25}$
HgS . . .	$9\cdot0 \times 10^{-32}$	$1\cdot0 \times 10^{-53}$	$9\cdot0 \times 10^{-31}$

The different values obtained by different investigators is very striking. A factor of great importance is the size of the particles composing the precipitate, as it has been shown—in the case of $BaSO_4$, for example—that the solubility increases as the size of the particles becomes smaller. It is evident that a considerable amount of useful work still remains to be done in this department of analytical chemistry. It should be pointed out that the relation, *viz.* equality between the solubility of an "insoluble" salt in water and the square root of its solubility product, only holds strictly if *hydrolysis* is negligible.

As supplementing the solubility table above, given in the case of sulphides, the following values for a few commonly occurring sparingly soluble halides and $PbSO_4$ are quoted. Temperature 25° C.

Salt.	Solubility in Water in Equivalents per liter.	Solubility Product L.
$AgCl$ . .	$1{\cdot}25 \times 10^{-5}$	$1{\cdot}56 \times 10^{-10}$
$AgBr$ . .	$6{\cdot}6 \times 10^{-7}$	$4{\cdot}35 \times 10^{-13}$
AgI . . .	$1{\cdot}0 \times 10^{-8}$	$1{\cdot}0 \times 10^{-16}$
$PbSO_4$ . .	$1{\cdot}5 \times 10^{-4}$	$2{\cdot}2 \times 10^{-8}$

It is evident from the foregoing considerations that a salt, such as $BaSO_4$, which is very sparingly soluble in water, possessing therefore an extremely small ionic product and at the same time containing acid and basic constituents which are *strong*, will not be dissolved except to an infinitesimal extent on adding even a strong acid (or a strong base). Thus, on adding acid to $BaSO_4$ (in suspension, say) the quantity of $H^{\cdot}$ which can be introduced, even as a maximum, is not great enough to cause the $H^{\cdot}$ and SO_4'' to unite to form undissociated H_2SO_4 except to an infinitesimal extent, for this acid being a very strong one is itself largely dissociated into ions.

Heterogeneous Hydrolytic Equilibrium.—What has been said above in connection with weak anions holds equally well with regard to weak cations. We have an illustration of this in a special case of *heterogeneous hydrolytic equilibria* in which the base is weak and the acid strong, *viz.* diphenylamine picrate, which hydrolyses into picric acid and diphenylammonium hydroxide. This base (or, as it is usually taken to be, simply diphenylamine) is practically insoluble in water. That is to say, its active mass is constant; similarly diphenylamine picrate is insoluble, and the hydrolytic expression—

$$\text{salt} + \text{water} \rightleftarrows \text{acid} + \text{base}$$

yields when the law of mass action is applied—

$$C_{\text{acid}} = \text{constant.}$$

Hence, if to a hydrolysed diphenylamine picrate solution some picric acid is added, the system will so change as to retain the acid at its (original) concentration previous to the addition. This can evidently only take place by some solid diphenylamine picrate being precipitated from solution. The system and its behaviour is exactly analogous to the $CaCO_3$, CaO, CO_2 gaseous equilibrium. Notice also if in this latter system CO_2 at *less* than the equilibrium pressure be brought into contact with CaO no $CaCO_3$ is formed, so if picric acid at less than the equilbrium concentration be brought into contact with diphenylamine no picrate is formed. This can be shown by the different colour effects produced, for picric acid itself is yellow, diphenylamine is colourless, and the picrate is brown. On adding picric acid containing 14 grams per liter at 40·6° C. to the diphenylamine, the base is stained brown owing to formation of picrate. If the solution of acid contains 13 grams per liter no coloration is produced.

This startling behaviour and its dependence on the fact that the picric acid must have a constant concentration at a given temperature, should be compared with the analogous hydrolytic reaction in which picrate of urea, which is only sparingly soluble in water, hydrolyses, giving rise to urea and picric acid. The law of mass action requires that $\frac{C_{acid} \times C_{urea}}{C_{salt} \times C_{H_2O}}$ shall be constant, or $C_{urea} \times C_{picric\ acid} = \text{constant}$, *both* of these being easily soluble in water. If we take this system and add picric acid, the result is that there is a permanent increase in picric acid concentration (compared with the initial concentration value), but at the same time some of the urea disappears from solution, having been transformed into picrate of urea, which is sparingly soluble, some of which is therefore precipitated. The case is analogous to the gaseous dissociation of solid ammonium hydrosulphide.

For further details of the above the student is referred to J. Walker and J. R. Appleyard, *Picric Acid and Diphenylamine* (*Trans. Chem. Soc.*, **69**, 1341, 1896). For heterogeneous equilibria between electrolytes in general, the student is referred to Abegg's *Theory of Electrolytic Dissociation*. Having discussed and illustrated the *principle* of the mutual action of ions upon one another in so far as it affects the solubility of salts, it is necessary to consider more precisely what *rôle* is played by the undissociated portion and how far the above generalisation is true.

RECENT WORK ON THE SOLUBILITY PRODUCT.

(Noyes and collaborators, *Journ. Amer. Chem. Soc.*, **33**, 1643, 1911.)

Noyes in the introduction to the experimental investigation, which deals largely with thallium salts, states the position of the problem as follows.

The following well-known solubility principles were originally formulated upon the basis of the law of mass action:—

I. The product of the concentration of the ions of a salt present as solid phase has the same value in dilute solutions of other salts as it has when it is present alone (Nernst, *Zeitsch. physik. Chem.*, **4**, 379, 1889).

II. The concentration of the un-ionised portion of a salt present as solid phase has the same value in dilute solutions of other salts as it has when present alone (A. A. Noyes, *Zeitsch. physik. Chem.*, **6**, 243, 1890).

It was, however, early recognised that both of these principles cannot hold true accurately, since the ionisation of salts (as derived from the conductance ratio $\left(\frac{\Lambda_v}{\Lambda_\infty}\right)$ or freezing-point lowering) does not change with the concentration in accordance with the law of mass action [*i.e.* Ostwald's dilution law does not hold]. The first principle has been generally employed, since it was shown by Arrhenius that the second of the above principles is not even approximately true (*Zeitsch. physik. Chem.*, **31**, 224, 1899). Thus Arrhenius showed that in the data obtained by Noyes for the solubility of TlCl, the solubility of the TlCl, namely (0·00170 N) in presence of 0·8 N KCl, is *less* than the undissociated part of TlCl (*viz.* 0·00179 N) when no KCl is present. Arrhenius found the same thing in connection with the solubility of silver salts of organic acids in presence of a common ion, the concentration of the un-ionised part decreasing rapidly with increasing concentration of the common ion, even beyond the point at which the total solubility became less than the concentration of the un-ionised portion in pure water. Stieglitz (*Journ. Amer. Chem. Soc.*, **30**, 946, 1908) concluded from a further study of the same data, that the first principle expressing the constancy of the product of the ion-concentrations is approximately true for these uni-univalent[1] silver salts, and suggested that this might be adopted for the present as an approximate empirical principle. Recent computations have shown, however, that the first principle is also subject to considerable deviations, and that these lie in a direction opposite to that of the deviations from the second principle. Thus it has been computed (Noyes, *Zeitsch. physik. Chem.*, **52**, 636, 1905) that in a solution saturated at 40° C., both with thallous chloride and thallous thiocyanate, where the total concentration is about 0·04 N, the concentration of the un-ionised TlCl is about 15 per cent. less, and the product of the concentration of the $Tl^{\cdot}$ and Cl' ions about 5 per cent. greater than it is in a solution of thallous chloride alone.

"Any such computations necessarily involve some principle in regard to the ionisation of salts in mixtures. Assuming that the conductance-ratio $\frac{\Lambda}{\Lambda_0}$ is an accurate measure of ionisation, the following principle, first stated by Arrhenius,[2] has been well established in the case of uni-univalent salts through the study of the conductance of mixtures of them, *viz.*[3] in a mixture of two salts with a common ion, each salt has a degree of ionisation equal to that which it has when alone present in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture. This principle when combined with the empirical law, which has been found to express the change of the ionisation $a = \frac{\Lambda}{\Lambda_0}$ of single salts, with the concentration (C)—

---

[1] This is Noyes' nomenclature for indicating the valences of the constituent ions of salts, *e.g.* AgCl is a uni-univalent salt, Ag_2SO_4 is a uni-bivalent salt, $PbSO_4$ is a bi-bivalent salt, $AlCl_3$ is a tri-univalent salt, and so on.

[2] *Zeitsch. physik. Chem.*, **2**, 285, 1888; **31**, 218, 1899.

[3] For references, see Sherrill, *Journ. Amer. Chem. Soc.*, **32**, 741, 1910.

$$\frac{(Ca)^n}{C(1 - a)} = K \quad . \quad . \quad . \quad . \quad . \quad (1)$$

may be expressed mathematically by the following equation[1]:—

$$\frac{C_{B+}C_{A-}}{C_{BA}} = K(\Sigma C_i)^{2-n} \quad . \quad . \quad . \quad . \quad (2)$$

where K is a constant characteristic of the salt, C_{B+} and C_{A-} are the concentrations of the positive and negative ions, of a salt BA, C_{BA} that of the un-ionised portion of the salt, and ΣC_i denotes the sum of the equivalent concentrations of all the positive or negative ions present in the solution, a quantity which will hereafter be called the total ion-concentration. The exponent n has a value lying almost always between 1·40 and 1·60.

"In applying this equation (2) to any special mixture the values of a, ΣC_i, n and K are first determined for each salt from the conductance data for the salt, and the values of C_{B+}, C_{A-} and C_{AB} for each salt in the mixture and of ΣC_i are then computed from the equation by a method of approximation.[2] In mixtures with a common ion it is only necessary to know the relation between a and ΣC_i for each salt, since the above ionisation rule may then be applied directly. In mixtures without a common ion the relation of the function $\frac{C_{B+}C_{A-}}{C_{BA}}$ to ΣC_i is determined for the separate salts, and is then applied for calculating the concentrations in the mixture.

"It is important to note that the only evidence in favour of equation (2) is that the specific conductances of mixtures calculated with its aid are in good agreement with the experimental values. It therefore will furnish correct values of the ion-concentrations only in case the commonly accepted principle is correct, that the conductance ratio $\frac{\Lambda}{\Lambda_0}$ is a reliable measure of the degree of ionisation of a single salt, a principle which can be true only in case the mobilities of the ions do not vary with the concentration.

"In the case of salts of the uni-bivalent type, there is, furthermore, the uncertainty as to whether intermediate ions (such as KSO_4^- or NO_3Ba^+) are present in considerable proportions.

"This 'un-ionised' concentration and this 'solubility product' should, according to the mass action law, be constant in any saturated solution. The actual variations of these quantities in the different cases are shown in the last two columns of the table. In every case the un-ionised concentration (BA) *decreases* markedly and the solubility

---

[1] Arrhenius, *Zeitsch. physik. Chem.*, 31, 218, 1899. Sherrill, *loc. cit.*

[2] For examples see *Journ. Amer. Chem. Soc.*, 32, 741, 1910; 31, 754, 1909.

SATURATED TlCl SOLUTIONS. SOME RESULTS.

Added Salt (KCl).	(ΣTl.)	(Σi.)	(K^+.)	(Tl^+.)	(Cl^-.)	(½Ba^{++}.)	(½$BaCl_2$.)	(KCl.)	(TlCl) (Undissociated Salt.)	(Tl^+)(Cl^-) (Ionic Product).
0·0	16·07	14·32	0·0	14·32	14·32	—	—	0·0	1·755	204·9
25·0	8·69	29·88	22·58	7·30	29·88	—	—	2·42	1·390	218·1
50·0	5·90	48·85	44·15	4·70	48·85	—	—	5·85	1·204	229·6
100·0	3·96	88·40	85·5	2·90	88·40	—	—	14·5	1·061	256·3
200·0	2·68	166·54	164·8	1·74	166·54	—	—	35·2	0·94	290·0
(½$BaCl_2$) added.										
0·0	16·07	14·32	—	14·32	14·32	0·0	0·0	—	1·755	204·9
25·0	8·98	28·00	—	7·59	28·00	20·41	4·59	—	1·392	212·5
50·0	6·18	44·30	—	4·98	44·30	39·32	10·68	—	1·203	220·6
100·0	4·16	77·97	—	3·11	77·97	74·86	25·14	—	1·052	242·4
200·0	2·82	142·7	—	1·89	142·7	140·8	59·2	—	0·93	270·0

product (B^+)(A^-) *increases* slightly, as the total concentrations of the salts and of the ions in the saturated solution increase."

In the case of very insoluble substances, such as the metallic sulphides of Groups I. and II., and the silver halides, etc., the simple view already expounded regarding the constancy of the ionic product in presence of moderately dilute solutions (reagents) containing ions common to precipitated substance and precipitating agent, may still be regarded as very nearly true. For further details upon the very important bearing of physico-chemical principles upon problems in analytical chemistry, the reader is referred to Wilhelm Ostwald's *Foundations of Analytical Chemistry*, translated by McGowan, or the more recent work of Stieglitz, *Elements of Qualitative Chemical Analysis*.

As regards the problem of the solubility relations of easily soluble salts in their action upon one another's solubility very little is as yet known. The difficulty is that in concentrated solutions such as are met with in these cases, it is no longer justifiable to attempt to apply relationships deduced for dilute solutions. The relation between the osmotic pressure and the concentration, for example, is no longer one simply of direct proportionality. There is a great deal of scope for investigation here. Since no wide generalisations have as yet come to light, it must suffice to simply refer the reader to a paper by J. Irvine O. Masson (*Trans. Chem. Soc.*, **99**, 1131, 1912), in which such solubility problems are dealt with. For work on solubility in general the reader is referred to V. Rothmund's *Löslichkeit und Löslichkeitbeinflüssung* (Bredig's Series of Textbooks).

CHAPTER VIII.

Chemical equilibrium in heterogeneous systems modified by capillary and electrocapillary effects—Colloidal solutions.

In this chapter it is proposed to consider the properties and conditions of equilibria which one finds in pseudo-solutions such as suspensions, emulsions, and colloidal solutions. The thermodynamic treatment of the process of adsorption at the interface between two phases will be considered in Vol. II., Chap. XI.

SUSPENSIONS, EMULSIONS, COLLOIDAL SOLUTIONS.

These all represent types of pseudo-solution. They differ from true solutions in that with suitable microscopic or ultramicroscopic apparatus it is possible to distinguish the individual particles of the "solute," which it is impossible to do in the case of solutes such as sodium chloride, etc. To the first class of substances which do not form true solution, *i.e.* substances in which the process of disaggregation does not reach the molecular limit when brought into contact with a liquid, Graham gave the name *colloids* to distinguish them from substances such as NaCl, urea, etc., to which he gave the name *crystalloids*. The first class of substances gives rise to heterogeneous solutions, the second class to homogeneous solutions. It must be remembered, however, that the transition between the two kinds of solution is gradual and not sharp. In fact, it is by no means easy to define exactly from this standpoint what we mean by a homogeneous solution unless we use a series of properties possessed by the one and not possessed (or only partially possessed) by the other type as arbitrary criteria. To show that the transition between the two classes is gradual one may consider the property known as the Tyndall optical effect. When a beam of light is passed in a given direction through a medium containing fine particles in suspension the light is reflected from the particles, which are thereby made luminous and is partially polarised if observations are made at right angles to the direction of the beam. This phenomenon is exhibited by all colloidal solutions. It is not exhibited by true solutions, at least in ordinary dilutions. Cane sugar solutions, however, when very concentrated, exhibit the phenomenon, though a dilute solution of cane sugar is a typically homogeneous one. Suspensions, emulsions, and colloidal solutions differ as regards the size of particles—at least this is the only distinction so far made. It is doubtful, however, whether suspensions such as that of kaolin in water are really stable, *i.e.*

whether they will remain in suspension for infinite time as colloidal solutions such as gelatine would certainly do, so far as our knowledge goes. Graham, as a matter of fact, regarded even colloidal solutions as really unstable, *i.e.* the colloid was in the act of precipitating itself, the process being an extremely slow one due to the smallness of the particles and the viscosity of the liquid medium. As regards our knowledge of these phenomena from the historical standpoint it is not necessary to say much, except to note that Graham, in 1862, was the first to study them scientifically and (as already mentioned) originated the name colloid. Graham's attention was drawn to this class of substances as a result of his experiments on diffusion of substances in solution (in water) through animal membranes. He found that while substances like common salt diffused readily, other substances like gelatin, albumin, silicic acid, did not pass through. He further found that solutions of these latter substances were very sensitive to the presence of acids and salts. He found, for example, that silicic acid or albumin could be precipitated from "solution" on adding a very small amount of HCl. Since the introduction of the electrolytic dissociation theory this effect has naturally been ascribed to the ions of the acid, base, or salt, and we shall study this more closely later. To the solution or pseudo-solution of silicic acid and other colloids Graham gave the name *sol*, and to the substance after precipitation the name *gel*, since as a rule colloids assume the form of a gelatinous mass after being precipitated as above.

As examples of suspensions we may take kaolin or sulphur in water, or indeed any very finely divided solid. Emulsions consist generally of liquid particles distributed through a medium, *e.g.* milk (which consists of small particles of fat in suspension in water), rubber latex, and oil emulsions, which are obtained on vigorously shaking up a small quantity of an oil with water, or by dissolving the oil in a little alcohol and pouring the whole into water. To colloidal solutions belong substances such as starch, albumin, gelatin, silicic acid, many dyestuffs, certain hydroxides such as $(Fe(OH)_3)_n$, certain sulphides such as $(As_2S_3)_n$, metals such as platinum in water. Colloidal solutions of metals are obtained most easily by Bredig's method of sparking electrodes of the metal under the surface of water, or by reduction of a salt to the metallic state, say, by formaldehyde.

Besides colloidal solutions in which water is the liquid medium, Svedberg (notably) has succeeded in preparing colloidal substances in organic solvents. Thus colloidal platinum can be prepared in the following solvents: amyl and ethyl acetates, the alcohols, acetone, ether, chloroform. Carbon and silicon form stable colloidal solutions in the higher alcohols. Pb, Sn, Zn form stable solutions in ethyl acetate and acetone. Cerium in isobutyl alcohol; Pt and Pd are also stable in isobutyl alcohol. For details the reader should consult Svedberg's book on the preparation of colloidal substances (*Herstellung Kolloider Lösungen*, Dresden, 1909).

At this point reference may be made to the work of P. P. von

Weimarn (*Zur Lehre von den Zuständen der Materie*, 1914, and *Grundzüge der Dispersoidchemie*, 1911), who considers that any substance may be obtained in the colloidal state, provided the correct conditions prevail. Von Weimarn emphasises the idea of the colloidal state, as a general conception, rather than the more limited idea conveyed by the term, a colloidal substance. Von Weimarn's theoretical treatment of the problem is of a very general nature. It is concerned with the formation of precipitates in varying degrees of fineness or dispersion. In this connection von Weimarn introduces what he calls a "law of corresponding states" for the process of crystallisation. To appreciate this point it is necessary to define a term called the ***dispersion coefficient***, represented by the symbol δ. If we mix two substances together in solution, which react to give a very soluble substance together with a slightly soluble substance, the physical characteristics of the precipitate of the latter are defined, according to von Weimarn, by the term δ, the dispersion coefficient of the precipitate. In the simplest case δ is given by the expression—

$$\delta = \frac{C}{S} \cdot \eta$$

in which S is the solubility of the slightly soluble substance (measured in the ordinary way), in equivalents per liter, C the concentration in equivalents per liter of the amount of the slightly soluble substance "potentially" present in the solution per liter, prior to precipitation. This quantity must be precipitated in order that the limiting value S may be reached. η is the viscosity of the solution. It will be observed that the greater is, C, that is the greater the degree of "potential" supersaturation of the solution with respect to the slightly soluble substance, the greater will δ be; that is, the finer grained is the precipitate formed. A small value of δ means, therefore, large grain or crystal formation. This is known to be in general agreement with experiment. It will be further observed that in the above expression we deal simply with numerical quantities. Von Weimarn was led consequently to generalise the expression in the following way: the physical characteristics of *any* precipitate will be the same provided the precipitation has taken place under "corresponding states" or conditions; that is, when the term $\frac{C}{S}\eta$ is the same for the various reactions. The term C/S is called the degree of supersaturation of the solution. By making use of this simple idea von Weimarn has succeeded in preparing precipitates of numerous substances, *e.g.* NaCl, $BaSO_4$, AgCl, in all degrees of fineness from coarse obviously crystalline structures to colloidal jellies. Analytical chemical experience has shown in a qualitative way that many precipitates, notably $BaSO_4$, can be obtained in very different degrees of fineness. We shall therefore take the case of $BaSO_4$ as an illustration of the precision and control which von Weimarn has introduced into the production of this precipitate under different physical conditions.

To prepare the precipitate von Weimarn mixes a solution of $Ba(CNS)_2$ and a solution of $MnSO_4$. These solutions are of equal volume, and at the same equivalent concentration. The concentrations employed varied over the range from N/20000 to 7 N, the volumes being always so chosen that, volume × concentration = constant. That is, the same total amount of $BaSO_4$ is precipitated in every case. It is obvious that extremely large volumes must be employed in the case of the most dilute solutions. Under these conditions the results are strictly comparable. To systematise the results it has been found convenient to divide the series of concentrations into groups. Throughout one group the ratio C/S alters by a known amount. The following is a brief summary of some of the results obtained:—

Group I. Concentration range: N/20000 to N/7000. C/S, 0 to 3, *i.e.* a very small degree of supersaturation.

Under these conditions, very slow crystallisation takes place around the condensation nuclei (dust particles), resulting finally in the formation of relatively large crystals. The time required is very long, several years being necessary for precipitation in the case of the most dilute solutions.

Group II. Concentration range: N/7000 to N/600. C/S, 3 to 48.

In this case the precipitate consists of a fine powder, which under the microscope is seen to be definitely crystalline. With N/5000 the precipitate appears after a month has elapsed, the time decreasing rapidly as initial concentration is increased, until, with N/1000 the solution becomes opalescent in the course of five minutes, and precipitation goes on for 2-3 hours. The greater the concentration, the finer the precipitate.

Group III. Concentration range: N/600 to 3 N. C/S, 48 to 88000.

As the concentration increases, the precipitate, which is at first granular, becomes curdy and finally gelatinous. This last stage, which is usually spoken of as amorphous, is, according to von Weimarn, composed of ultra-microscopic crystals.

Group IV. Concentration range: 3N to 7N. C/S, 88000 to 200000.

In this case, if the $Ba(CNS)_2$ solution be allowed to fall in drops into the $MnSO_4$ solution, each drop is covered by a gelatinous layer or membrane, which eventually falls to pieces as a flocculent precipitate. With 5N solutions the drops settle to the bottom, and if the solution be stirred, it sets to a viscous jelly. This jelly is not permanent, however, changing eventually to the flocculent precipitate. The drops referred to, with their coating of jelly, if undisturbed, exhibit the phenomenon of swelling or imbibition which is referred to later. It is this swelling which eventually causes the destruction of the sac and the formation of the flocculent precipitate.

It is evident from these results that a colloid gel stage may be expected in all cases of precipitation, although it may be so transient as not to be observable. The action of certain colloids in the electrodeposition of metals, referred to later, is probably connected with a transient colloid state of the metal in the act of precipitation.

It will be recognised that many of the colloidal precipitates obtained by the above procedure are not stable, passing into a powdery form. This is a usual experience in analytical work. It arises from the fact that the solubility of a very finely divided precipitate, is greater than that of the coarse form. The fine particles may therefore re-dissolve and become precipitated upon other larger nuclei. This is due to the fact that the surface tension of a small sphere is less than that of a large, which means in turn that the vapour pressure and the solubility are greater in the case of the small sphere than in the case of the large. Lord Kelvin first showed, on this basis, why it is that in a mixture of large and small rain drops, the large increase in size at the expense of the small. Any irregularity in size tends therefore to cause the precipitate to become coarser.

To maintain the precipitate in as fine or colloidal a state as possible, it is necessary to make C/S as large as possible. This can be effected by decreasing S, say by the addition of alcohol to the water in the above case, for $BaSO_4$ is less soluble in alcohol than in water. The recrystallisation process will then be retarded, and the colloidal form remains more or less stable.

From this brief account it will be evident that von Weimarn has succeeded in defining and controlling the process of precipitation in a striking manner. This is an important matter, although of course it by no means covers all the phenomena exhibited by the colloidal state.

In the writer's opinion it would not be justifiable to conclude from the above observations and considerations that the colloidal state proper is always one of ultra-microscopic *crystalline* structure. This may be the case in such substances as salts, though even here it is doubtful. In other cases, such as gelatin, albumin, starch, and in the case of oil emulsions we have nothing to do with crystalline form in these systems as ordinarily produced. To return to the characteristics of colloidal solutions, which are of course shared to different degrees by emulsions and suspensions, one may note the following: rate of diffusion, osmotic pressure, optical properties. These effects give us an indication of the size of the particles. Other characteristics are: the Brownian movement, the electric charge on the particles, and the phenomena of cataphoresis and endosmose, coagulation phenomena and protective effect (peptisation), ferment action of colloidal metals. We shall consider these points in some detail.

DIFFUSION AND OSMOTIC PRESSURE.

As already mentioned in connection with Graham's work, colloids as a whole do not diffuse, or at most only slowly. Their osmotic pressure is also extremely small. The fact that the osmotic pressure is so small is shown by attempts made to measure it directly, and also by the lowering of vapour pressure of the solution and the lowering of the freezing point of water, say on adding substances such as starch or gelatin. Only an extremely small effect is observed, and as may be shown on thermodynamic grounds, small vapour pressure changes and freezing-point changes correspond to a small concentration or osmotic pressure, if indeed it is allowable to speak of concentration in the case of a solution which is heterogeneous. Measurements made have thus led to enormous values for the molecular weights of these bodies when in solution, *e.g.* :—

	M		M
Gelatin . .	5000	Gutta-percha[1] .	40,000
Dextrin . .	1083	Tungstic acid .	1750
Starch . .	25,000	Tannin . . .	3000
Albumin . .	14,700	Ferric hydroxide .	6000

It must be remembered that if the colloid is not pure—if, for example, it contains some electrolyte (as is frequently the case with dyestuffs prepared in the ordinary way by "salting out" by means of the electrolyte), even after prolonged dialysis—quite measurable osmotic pressure may be observed. This has been investigated especially by B. Moore, by Bayliss, and by Donnan. It is a well-established fact that many colloids of physiological origin can scarcely be freed from the electrolytes (NaCl) which accompany them in the tissues. So close is the adherence of these electrolytes to the colloid that it is customary to look upon the impure colloid as a loose chemical compound of colloid + electrolyte. The investigations of Moore and Roaf (*Biochem. Journal*) are among the most important in connection with this subject. For a discussion of "forced membrane hydrolysis" and membrane equilibria, in which it is shown that an electrolyte such as NaCl does *not* distribute itself at equal concentrations on both sides of a parchment membrane when congo red is present on one side, a paper by Donnan and Harris (*Trans. Chem. Soc.*, **99**, 1554, 1911) should be consulted. Donnan's theory of such distribution effects is considered in Vol. II., Chap. XI.

OPTICAL PROPERTIES.

As regards optical properties of colloidal solutions that known as the Tyndall effect already mentioned is the most striking. It shows the existence of heterogeneity in a very direct manner. Attempts have also frequently been made to observe the particles and estimate their size by means of the microscope. This is not a difficult thing in the case of suspensions and emulsions. It fails, however, in the case of colloidal solutions such as those mentioned, owing to the small size of the particles. This has been overcome, however, in a very ingenious manner by Siedentopf and Zsigmondy by means of their ultramicroscope. In this instrument the field of view (of an ordinary good microscope) is kept dark and light enters transversely, *i.e.* horizontally. The tiny particles cause reflection of the light, giving rise to images which are large enough to be visible and appear as bright, rapidly moving patches of light accompanied by diffraction rings in the microscope eyepiece. By this method, therefore, we are able to demonstrate the presence of extremely small particles; but, of course, we do not discern the actual particles themselves.

---

[1] *Cf.* Caspari, *Trans. Chem. Soc.*, **105**, 2139, 1914.

THE SIZE OF THE PARTICLES IN EMULSIONS AND COLLOIDAL SOLUTIONS.

In the case of suspensions, the diameter of the particles as shown by an ordinary good microscope is mainly of the order 10^{-3} cm., though a considerable number of the particles are usually much smaller. Suspensions are as a rule very uneven.

In the case of emulsions, V. Henri has shown by the same means that rubber latex particles have a diameter between 10^{-4} and 10^{-5} cm. Lewis (*Zeitsch. Koll.*, **4**, 211, 1909) also showed that the diameter of hydrocarbon oil emulsion particles in water is approximately 4×10^{-5} cm. It was roughly shown also that this appeared to be a *critical* size, *i.e.* an equilibrial size, in the following way: An emulsion was prepared by boiling a small drop of oil for many hours with a large quantity of water. The size of the particles was of the same order as in the emulsion prepared by vigorous shaking. A similar (and much more even) grained emulsion was obtained by dissolving the oil in a little alcohol and pouring the mixture into water. The diameter of the particles was again observed to be about 4×10^{-5} cm. In the previous methods this size of grain was reached by breaking down large masses; by the latter method the same value was reached by a process of limited coagulation from individuals of molecular size (oil molecules dissolved in alcohol form a "true" solution). It may also be mentioned that the milky emulsion formed in the receiver on distilling aniline in steam possesses grains of which the majority are of the order 10^{-5} cm. in diameter. Rapid coagulation to a "massive" oil layer takes place in this case, however, so that the emulsion is not a very stable one. This order of magnitude 10^{-5} is that predicted as an approximate result by Donnan on the basis of his thermodynamic theory (*Zeitsch. physik. Chem.*, **46**, 197, 1903).

In the case of colloidal solutions the microscope, as already mentioned, is of no use. Thus Bredig showed that as a result of the ***invisibility*** of colloidal gold particles in water when viewed by a microscope, that the particles must have a diameter less than $0{\cdot}14\ \mu$ ($1\ \mu = 10^{-4}$ cm.). Lobry de Bruyn considered that colloidal particles would not have a diameter *less* than 5-10 $\mu\mu$ ($1\ \mu\mu = 10^{-7}$ cm.), since smaller particles would not polarise light. A closer approximation may be obtained on the basis of the electromagnetic theory of light, according to which the wave-length λ, which suffers maximum absorption on passing through the colloidal solution, is connected with r, the radius of the colloid particle, by the relation—

$$r = \frac{\sqrt{3}}{4\pi n} \cdot \lambda$$

where n = refractive index of the medium (water). For colloidal gold solutions the maximum absorption occurred at λ 490-520 $\mu\mu$. And hence r is $4{\cdot}9$ to $5{\cdot}2 \times 10^{-6}$ cm. (10^{-6} cm. = 10 $\mu\mu$). Similarly in the case of colloidal platinum, r comes out to be $4{\cdot}8 \times 10^{-6}$ cm., and for colloidal silver $(3{\cdot}8$ to $4{\cdot}8) \times 10^{-6}$ cm. Sir Joseph Thomson from other optical considerations (*cf. Recent Researches in Electricity and Magnetism*, p. 437) obtained a similar order of magnitude. Pockels and Zsigmondy and others, however, have come to the conclusion that the absorption band method is dependent on other factors, such as the shape of the particles and their chemical nature.

The most accurate method is by means of the ultra-microscope. The number of particles contained in a certain volume of solution can be counted, and the metal estimated by evaporating a certain much larger amount of solution and weighing the metal. Assuming the density of the particles to be approximately the same as that of the massive metal (in the ordinary form) the volume of each particle and hence the radius can be determined. In this way for colloidal gold particles (obtained by Bredig's sparking method) it has been found that r = $2\text{-}8 \times 10^{-6}$ cm., for silver $r = 5\text{-}7{\cdot}7 \times 10^{-6}$ cm.; for Pt, $r = 4{\cdot}4 \times 10^{-6}$ cm.; for colloidal silver iodide $r = 6 \times 10^{-6}$ to 1×10^{-4} cm.; this latter is not stable, however, and assumes the gel form in a few days. As a rule particles greater than 10^{-6} coagulate after a short time.

THE BROWNIAN MOVEMENT.

The botanist Brown, in 1827, observed that fine suspensions and even very small gas bubbles suspended in a liquid medium are in a continuous state of vibration to and fro and up and down. This has been also observed for emulsion particles and still more for particles in colloidal solutions. The smaller the particles the greater the Brownian movement. It was first suggested by Ramsay and later by Gouy, and it has been conclusively proved in recent years by Perrin, that this is due to the collisions of the colloidal particles with the molecules of the medium (say water). And, indeed, he has employed this in a most ingenious manner to calculate the number of molecules in a gram molecule, as we have already seen (*cf.* Chap. I.).

THE ELECTRIC CHARGE ON THE PARTICLES.

That the particles in suspensions, emulsions, and colloidal solutions possess an electric charge is easily shown by placing the liquid in a U tube fitted with electrodes charged to a fairly high potential difference, when it will be found that the particles wander to one of the poles, *i.e* the so-called cataphoresis phenomenon.[1] In this way it has been shown that the particles possess either a positive or negative charge; the majority being charged negatively when water is the medium. This is in agreement with the rule that when two substances are electrified by friction the substance with the higher dielectric constant takes on a *positive* charge, the other being negatively charged. Water has a very high dielectric constant, and hence if we regard the origin of the charge on the particles as similar to frictional electricity, one would expect the water as a rule to be positive. As regards the charge carried by *suspensions*, Quincke showed in 1861 that the following substances in water travelled with the current, *i.e.* were *positively* charged (the water being negative): Quartz, kaolin, sulphur, lycopodium, air bubbles and bubbles of ethylene. [The results with air bubbles are surprising and somewhat doubtful.] No measurement of the charge has been made in any of these cases.

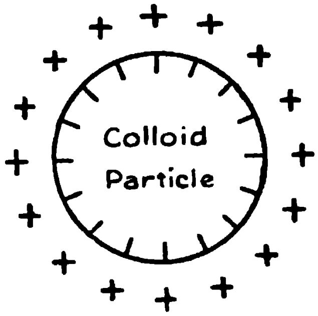


FIG. 50.—Illustrates the electric "double-layer". The positive charges are situated upon the molecules of the medium.

Lewis (*loc. cit.*) measured the velocity of movement of oil emulsion particles in water in an electric field, the potential difference between the electrodes being 230 volts. The hydrocarbon oil droplets are negatively charged, as are also mastic particles. According to the Helmholtz-Lamb theory of the "double layer" of (+) and (−) electricity formed by friction (*cf.* Fig. 50), the following relation holds :—

$$V = \frac{4\pi}{K}\frac{\eta v}{X}$$

where V is the P.D. between each particle and the water in contact with it.

K is the dielectric constant of water.

η is the viscosity of water.

v = velocity of the particle in centimetres per second under a P.D. gradient of X units per centimetre.

From this it was found that V = 0·05 volt for the emulsion oil particles suspended in water. Now we can write—

$$e = V\frac{r^2}{d}K$$

where e is the charge on the particle, d the thickness of the electrical double layer (which is supposed to be small compared to r, the radius of the particle). This formula will be referred to later. On substituting the data it is found that $e = 4 \times 10^{-4}$ *electrostatic units.* This should be compared with the values obtained for colloidal particles (see below).

---

[1] Endosmose is the reverse of cataphoresis. Endosmose denotes the movement of a liquid along the walls of a fixed tube when a P.D. is put on the ends.

In connection with cataphoresis it is necessary to realise that the movement of the colloid particle in an electric field is only made possible by the fact that there is a certain slip or "give" between the two coatings of the double electrical layer. If the charges were fixed the particle as a whole would have no effective charge and would therefore remain motionless in the electric field. The first stage in the act of cataphoresis must be, therefore, a polarisation of the colloid—medium system, followed by a transfer of the charge on the layer, made up of the molecules of the medium, to other contiguous molecules. In this way the colloid particle is handed on, so to speak, by the molecules of the medium. This slip of the charge, as we shall see later, is of importance in dealing with the determination of the magnitude of the charge as determined by the application of Stokes' Law.

We now pass on to consider *the electric charge carried by colloidal particles.* Investigation upon this subject was first undertaken by Linder and Picton (*Trans. Chem. Soc.*, 1892, p. 160). By the U-tube method already mentioned it has been shown that the following colloids (in water) are positively charged: hydroxides, *e.g.* $(Fe(OH)_3)_n$, methyl violet, methylene blue, magdala red, and other dyes. The following substances (in water) are negatively charged: colloidal metals, *e.g.* platinum, sulphur, sulphides, eosin, aniline blue, methylaniline green, indigo, silicic acid, stannic acid, resin, starch, silver halides, etc. Hardy (*Journn. Physiol.*, **24**, 288, 1899) showed that with albumen in a U tube in *alkali* a white coagulum collected at the anode, *i.e.* the colloid was negatively charged; whilst in *acid*, albumen is positively charged. In neutral solution it is practically stationary. This result obviously suggests that in the case of albumen, at any rate, the excess of $H^{\cdot}$ ion or $(OH)'$ is the determining factor. The sign of the charge on a given colloid depends to a large extent on the medium. Thus Billitzer has prepared (*Zeitsch. Koll.*, **1**, 226, 1906) colloidal platinum in chloroform and found the metal positively charged, while in water it is negatively charged. On using a U tube with both solutions present, on applying the e.m.f., colloidal platinum moved in opposite directions, meeting at the boundary of the water and chloroform interface.

One of the most satisfactory investigations carried out on the charges carried by colloids, and on the conditions of their removal, is due to E. F. Burton (*Phil. Mag.*, [6], **11**, 425; *ib.*, **12**, 47‸, 1906). The scope of his investigation may be briefly outlined.

Lamb (*Phil. Mag.*, p. 60, 1888) showed that the velocity of an isolated particle in an electric field is given by the expression—

$$v = X\frac{\rho}{\beta}$$

where v = velocity in centimetres per second.
X = potential gradient of the field in electrostatic units, *i.e.* fall of potential per centimetre.

ρ = density of the charge on the particle, *i.e.* the charge per square centimetre of surface.

β = is a small coefficient given by—

$$l = \frac{\eta}{\beta}$$

where l is called the "facility of slip" of the particle itself against the most immediate layer of molecules of the medium in which it is embedded. η is the viscosity of the medium.

Now $\rho = \frac{e}{4\pi r^2}$, where e is the charge on a particle, and r the radius of the particle (assumed to be spherical). Hence Lamb's expression may be written—

$$v = \frac{Xe}{4\pi r^2} \cdot \frac{l}{\eta}$$

or

$$Xe = 4\pi r^2 \eta v \cdot \frac{1}{l} \quad . \quad . \quad . \quad . \quad (1)$$

We consider the small spherical particle as a condenser with "concentric plates" d cms. apart where d is small compared with r. That is, we assume the existence of a Helmholtz double layer of electricity of opposite sign surrounding the particle.

Since d is supposed small compared with r, the expression for the capacity C of the condenser arrangement takes the form—

$$C = \frac{r^2 K}{d}$$

where K is the dielectric constant of the medium between the plates. Lippmann and others regard this as unity. Possibly a better approximation is to regard it as Burton does, as being that of the total medium itself, *i.e.* water say. Now if the P.D. between the particle and the medium, *i.e.* between the sides of the double layer, is V, we know that—

$$C = \frac{e}{V}$$

and therefore

$$e = V \cdot \frac{r^2}{d} \cdot K.$$

Substituting this value of e in (1), we get—

$$V\left(\frac{l}{d}\right) = \frac{4\pi}{K} \frac{\eta v}{X}.$$

Lamb (*l.c.*) has given reasons for believing that l and d are of the same order of magnitude (10^{-8} cms.), and Burton therefore regards $\frac{d}{l}$ = unity approximately. We have therefore

$$V = \frac{4\pi}{K} \frac{\eta v}{X}$$

which is the expression already employed on page 334. If the units on the right-hand side are electrostatic, in order to obtain V in volts we must multiply by the factor, $(300)^2$, since 1 electrostatic P.D. unit = 300 volts, and X and v *each* involve this factor. Using the U-tube method Burton found the following values for the velocity v:—

WATER AS MEDIUM.

Colloidal Substance.	Sign of Charge carried by Colloid.	Velocity in cms. per second under a Gradient of 1 volt per cm.
Pt	(−)	$20\cdot3 \times 10^{-5}$
Au	(−)	$21\cdot6$
Ag	(−)	$23\cdot6$
Bi (Probably *hydroxides*, though Burton does not so regard them) .	(+)	$11\cdot0$
Pb	(+)	$12\cdot0$
Fe	(+)	$19\cdot0$

The last three substances were the least stable, being precipitated from solution in a week.

ETHYL ALCOHOL AS MEDIUM.

Colloidal Substance.	Sign of Charge carried by Colloid.	Velocity in cms. per second under a Gradient of 1 volt per cm.
Pb Hydroxides probably	(+)	$4\cdot5 \times 10^{-5}$
Sn	(+)	$3\cdot6$
Zn	(+)	$2\cdot8$

Ag, Au, Pt, Bi, Fe, Cu could not be prepared in the form of stable solutions in ethyl alcohol.

METHYL ALCOHOL AS MEDIUM.

Colloidal Substance.	Sign of Charge carried by Colloid.	Velocity in cms. per second under a Gradient of 1 volt per cm.
Pb	(+)	22×10^{-5}
Bi	(+)	$10\cdot2$

ETHYL MALONATE AS MEDIUM.

Colloidal Substance.	Sign of Charge carried by Colloid.	Velocity in cms. per second under a Gradient of 1 volt per cm.
Pt	(−)	$2\cdot3 \times 10^{-5}$
Ag	(−)	$1\cdot7$
Au	(−)	$1\cdot4$

Bi, Pb, Zn, Fe could not be obtained as stable colloidal solutions.

Employing the equation given, Burton obtained the following values for the P.D. (V) between the particles and the respective media :—

V IN VOLTS.

Nature of Medium : Water.		Ethyl Malonate.	C_2H_5OH.	CH_3OH.
Colloid.	K = 80 Electrostatic Units.	K = 10·7.	K = 25·8.	K = 33.
Pt . . .	− 0·031	− 0·054	—	—
Au . . .	− 0·033	− 0·033	—	—
Ag . . .	− 0·036	− 0·040	—	—
Pb } hydroxides ? .	+ 0·018	—	+ 0·023	+ 0·044
Bi	+ 0·017	—	—	+ 0·022

(The *sign* (+ or −) denotes the sign of charge carried by the particles.)

Burton remarks on the similarity in the values for the P.D. in the different cases. The same order of magnitude was obtained by the writer for oil emulsion particles. It should be mentioned that according to Burton's measurements the size of the colloids was larger than that usually obtained by other workers. Burton found $r = 2$ to 5×10^{-5} cm. This does not come into the above expression for V, but does come into the calculation of e, the charge on the particle which is obtained by means of the expression

$$e = V \cdot \frac{r^2}{d} K.$$

Burton did not calculate this, but it may be of some interest to work out a single case on his data. Take platinum colloid in water.

$r = 2 \times 10^{-5}$ cm. (approx.)
$V = \frac{0·031}{300}$ electrostatic units
$d = 5 \times 10^{-8}$ (Helmholtz's approximate value)
$K = 80$ (electrostatic units)
whence $e = 8 \times 10^{-5}$ electrostatic units.

For colloidal silver practically the same value is obtained. Of course these are only extremely rough values. Our knowledge of d may be in error to a very large extent. Its value may be ten times greater than that given. $\frac{l}{d}$ may not be unity at all, and this would throw out the values for V. We might make another attempt to measure e by applying Stokes' Law[1] to the motion of the particle in the field (instead of employing Lamb's formula). Stokes' expression would be

$$e = \frac{6\pi\eta r v}{X}.$$

Taking the case of silver colloid (using Burton's data for r, v, and X) one obtains $e = 8 \times 10^{-8}$ electrostatic units. It is doubtful whether the difference between this and the above value is real or is due to accumulation of errors. It should be pointed out, however, that the discrepancy is probably real, there being considerable doubt as regards the applicability of Stokes' expression, if we mean by the term e the total charge on the particle. Thus it is obvious that unless the layers of the Helmholtz "double layer" are able to slip at least to some degree past one another, the particle as a whole would not move at all in an electric field, for perfectly fixed electrical layers of equal and opposite sign would be an enclosed system with no apparent charge at all. In the above case, in applying the expression Xe as the electric force acting on the particle, we regard the particle as a point charge with an effective charge value e. Since, however, the slip is by no means complete, the value of e given by the Stokes expression cannot be the total e on the particle which is given (approximately) on the basis of Lamb's formula, since the *facility of slip* is at least considered by Lamb, even though the allowance made for it may be approximate. It is probable, therefore, that the values of e given by Stokes' expression are really considerably less than the true value.

Burton has attempted to measure e by yet another method, depending on the amount of $Al^{\cdots}$ ion required to precipitate (or coagulate) a given amount of colloid. Before giving this method it will be necessary to consider the *coagulation phenomenon* itself (*vide infra*).

The Source of the Charge on Colloid Particles.

Up to this point we have regarded the source of the charge on colloid sols as essentially physical, analogous to the production of charge in frictional electricity. This serves to give a relatively simple picture of the phenomenon, and at the same time much of the evidence available—such as the fact that it is the substance with the higher dielectric capacity (water) which takes on the positive charge—is not in disagreement with this view. Recent investigation, however, appears to be leading to a different conclusion, the origin of the charge being attributed to the condensation or adsorption or loose chemical union of electrolytic ions upon the surface of the colloid particle or *sol.* This is considered to be the case even with colloidal metals, such as platinum, in pure water. It is difficult to see how it could be the case for a colloidal metal in such a medium as chloroform, which is scarcely regarded as being capable of giving rise to ions even in the minutest amount. This ionic adsorption view is in line, however, with the modern view of coagulation of colloids by ions, as we shall see later. Although the contrast between the frictional view and the ion-adsorption view of the origin of the charge is marked at the present time, the distinction may ultimately prove to be more apparent than real.

---

[1] *Cf.* W. C. McC. Lewis, *Zeitsch. Kolloide*, 4, 209, 1909.

As an indication of the kind of evidence upon which the ion-adsorption view of electrical charge is based, reference may be made in the first place to the observations of Hardy on albumin. It has already been mentioned that albumin in neutral solution is apparently uncharged, in alkaline solution negatively charged, and in acid solution positively charged. This is most easily explained by attributing the negative charge to the adsorption of OH' ions, the positive charge to the adsorption of $H^{\cdot}$ ions.

In the second place reference may be made to the investigations of Powis (*Trans. Chem. Soc.*, **107**, 818, 1915) on the preparation of colloidal ferric hydroxide either in the positively charged or negatively charged condition. Hitherto ferric hydroxide has been regarded as typically a positively charged colloid. Powis has shown, however, that the sign of the charge is a matter of the environment during the preparation. Colloidal solutions of ferric hydroxide are usually prepared by dialysing a solution of, say, ferric chloride. The resulting colloid is positively charged, which is attributed by Powis to the fact that under these conditions (in which the colloid is formed in the presence of a relatively large amount of ferric ion), this ion is preferentially adsorbed by the colloid particles and confers its charge upon the colloid. By proceeding in a different manner Powis has succeeded in preparing negatively charged ferric hydroxide; the method being to allow a dilute solution of ferric chloride to run slowly into a slight excess of a dilute solution of alkali hydroxide with constant shaking. The resulting negatively charged sol is quite stable. The charge in this case is attributed to adsorption of the OH' ions from the alkaline solution. This evidence is strongly in favour of the ion-adsorption view of the origin of the charge.

In the third place mention may be made of the work of Beans and Eastlack (*Journ. Amer. Chem. Soc.*, **37**, 2667, 1915) upon the preparation of colloidal metals, such as platinum, by the electrical sparking method of Bredig. As the method simply consists in allowing an electrical spark to pass under water between electrodes of the metal which it is desired to have in the sol form, it has generally been considered that this method gives rise to very pure solutions of the colloid, no extraneous materials being required. Colloidal platinum, palladium, gold and similar metals in pure water prepared by this method are negatively charged. Beans and Eastlack approach the problem of the origin of the charge from the point of view of the electrical conductivity exhibited by such colloidal solutions. A preliminary calculation based upon the known size, charge, and mobility of the particles in a colloidal solution of gold in water showed that the specific conductivity of the colloid itself should be of the order 10^{-10} reciprocal ohms. This is only 0·01 per cent. of the conductivity of water itself, so that if the colloidal solution simply consists of the finely divided metal in suspension in unchanged water, the conductivity of the solution should not be distinguishable from that of the water. This, however, is not the case. The solution exhibits a larger conductivity than that of the water. Further, there is a marked difference in the enhanced conductivity according to the metal employed. Thus, in the case of colloidal platinum, the increase in specific conductivity is eight times that observed in the case of gold. Beans and Eastlack connect this larger conductivity with the fact that colloidal platinum is more stable than colloidal gold. The idea is, that the greater stability of the colloidal platinum is due to the presence of small amounts of electrolyte formed by the oxidation of the metal at the high temperature reached locally in the sparking process. The presence of chloride, bromide, iodide, and hydroxyl ions have a marked stabilising influence upon these colloidal metals even when the electrolyte is extremely dilute (0·0001 normal), and this observation affords a convenient method of preparing such colloids in a stable form. It is very important to note that this stabilising action is dependent on the presence of the added electrolyte during the sparking process; the stabilising action is not observed in the case of gold which has already been sparked in pure water and the electrolyte subsequently added. This may be a perfectly general phenomenon, though it cannot be stated as such at the present time. The inference to be drawn from these experiments is, that even when the medium is quite pure—no electrolyte added—the stability of the colloid is dependent upon its power of adsorbing or combining with some negatively charged ion (anion)—probably a complex anion containing the metal itself, produced in the sparking process and conferring the conductivity upon the solution as a whole. If this view be accepted, it follows further, that a very minute trace of complex metallic anion is sufficient to stabilise the colloidal metal, for all attempts to detect gold in the filtrate after the coagulation of a colloidal gold solution gave negative results. Referring for a moment to the stabilising effect of certain anions above mentioned it is of importance to point out that all anions do not possess this property. Thus, fluorides, nitrates, chlorates, and sulphates appear to be inactive, suggesting that there is a definite specific effect entering into the act of adsorption. We must also remember that the cation of the electrolyte is necessarily present, and as we shall see in the following section, this cation will tend to bring about coagulation of the colloidal metal; that is, the effect of the cation opposes that of the anion.

As a general conclusion from the above investigation we are led to regard the sparking method of preparation as involving, in the first place, a purely physical thermo-mechanical disintegration of the metal. The resulting system may be either stable or unstable. This is therefore an incomplete statement of the process, and we shall only possess a satisfactory view of the process when we have solved the problem of the resulting stability. The view taken by Beans and Eastlack is that after the mechanical disintegration has taken place there is a subsequent reaction between the colloid particles and certain ions present in the surrounding medium, resulting in the formation of an adsorption complex negatively charged. The anion referred to fairly certainly contains the OH′ ion from the medium (water) itself. Granted, however, that traces of electrolytic ions combined somehow with the colloidal particles are the origin of the charge and at the same time the source of the stability, we are still faced with the problem of the cause of the marked selective effects manifested by different colloids with respect to certain anions. The problem is by no means settled, though the ion adsorption view would appear to be essentially the correct one.

COAGULATION OF COLLOIDS. THE HARDY-SCHULZE LAW.

It has been known for some time that on addition of a very small quantity of certain electrolytes to suspensions, emulsions, or colloids, the corresponding substances are thrown out of solution and form flocculent precipitates (gels), or in the case of oil emulsions, the oil collects as a layer on the surface.[1] It has been found that a certain minimum quantity of electrolyte is required to effect this. This quantity is far too small to make the process analogous to that of salting out, in which, as is well known, large quantities of the "salt" are required. Further, the operation seems to be of a very physical nature. Until quite recently it was considered to depend solely on the sign of the charge carried by the suspended particle and to be practically independent of its chemical nature. *The important generalisation is that ions carrying a charge of sign opposite to that carried by the colloid are the most active precipitants, and at the same time the higher the valency of the ion* (i.e. *the greater the number of unit charges upon it*) *the greater its precipitating action.*

This is known as the Hardy-Schulze Law. It might perhaps more legitimately be known as the Schulze-Linder-Picton-Hardy Law.[2]

This is brought out by the following example dealing with the relative coagulating power of electrolytes required to precipitate a certain amount of colloidal $(As_2S_3)_n$ in water. This colloid is negatively charged, and hence positive ions of high valency exert the maximum coagulating effect. The coagulating power is simply the reciprocal of the molar concentration of the electrolyte required to precipitate all the colloid in a given time. Large coagulating power, therefore, means that a very small quantity of the given electrolyte is required. The coagulating power of KI in the table is taken as unity.

The great effect of $Al^{\cdot\cdot\cdot}$ ion is here brought prominently into view. Similarly divalent ions such as $Zn^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, are next in order of effect, and monovalent ions are least effective. It is evident at the same time that the anion is having some kind of effect, *i.e.* KCl and KI are not identical in effect. The part played by the anion has never yet

---

[1] One of the earliest investigations upon this subject is that of Ramsay (*Proc. Geol. Soc.*, 1876) upon the effect of salts on the settling of mud.

[2] Linder and Picton, *loc. cit.* Hardy, *Zeitsch. physik. Chem.*, 33, 385, 1900. Schulze, *Journ. praktische Chem.*, 25, 431, 1882; *ib.*, 27, 320, 1884.

COAGULATION OF COLLOIDAL ARSENIC SULPHIDE.

Electrolyte.	Coagulating Power of Electrolyte.
KI	1·0
KCl	2·5
Na_2SO_4 . . .	2·5
$CaCl_2$ . . .	80
$MgCl_2$ . . .	182
$ZnSO_4$ . . .	60
Al_2Cl_6 . . .	1518
$Al_2(SO_4)_3$ . . .	957

been cleared up. It is easily seen from the table, however, that the presence of an anion such as SO_4'' neutralises to some extent the effect of the cation, and one divalent anion possesses a greater neutralising effect on the cation than two monovalent ions, *e.g.* compare the coagulating power of Al_2Cl_6 and $Al_2(SO_4)_3$.

If the colloid is positively charged then of course the negative ions of high valency are the most effective precipitants, the cations in such a case exerting a hindering or neutralising influence. This is shown by the following data obtained by H. Freundlich (*Zeitsch. physik. Chem.*, **44**, 129 to 160, 1903) in the case of colloidal ferric hydroxide, *i.e.* $(Fe(OH)_3)_n$, which is positively charged in water as ordinarily prepared (compare preceding section). Instead of giving coagulating power the table gives the reciprocal of this, *i.e.* the minimal equivalent quantities of electrolytes required to precipitate a given quantity of the colloid in a given time.

COAGULATION OF $(Fe(OH)_3)_n^+$.

Electrolyte.	Minimal Concentration of Electrolyte Required for Precipitation.
NaCl . . .	0·00925 mols per liter
KCl . . .	0·00903 ,, ,,
$BaCl_2/2$ . . .	0·00964 ,, ,,
KNO_3 . . .	0·0119 ,, ,,
$Ba(NO_3)_2/2$ . .	0·0140 ,, ,,
K_2SO_4 . . .	0·000204 ,, ,,
$MgSO_4$ . . .	0·000217 ,, ,,
H_2SO_4 . . .	0·0005 ,, ,,

It will be noted that K_2SO_4 has the greatest coagulating power, this being due to the strong divalent anion SO_4'', which is only slightly retarded in its action by the two monovalent cations $K^{\cdot}$. When, for example, $Ba^{\cdot\cdot}$ or Mg is substituted for $K^{\cdot}$ the coagulating effect of a given anion, say Cl', is retarded, *cf.* $BaCl_2$ and KCl. Whetham has generalised the coagulating effects approximately in the following statement, which he deduced on the basis of the theory of probability (*Phil. Mag.*, **48**, 474, 1889; *Zeitsch. physik. Chem.*, **33**, 385, 1900), namely: *The coagulating power* (i.e. *the reciprocal of the minimal concentration*) *of a series of ions of the same sign is proportional to a constant raised to the power representing the valency of each ion* (*Whetham's Law*). If the coagulating powers of a mono-, di- and trivalent radicle are P_1, P_2, P_3, then

$$P_1 : P_2 : P_3 = K : K^2 : K^3.$$

This, however, does not allow quantitatively for the apparent effect of the oppositely charged ion, which of course is always present.

As regards the *kind* of union which takes place between the active ion and the colloid, practically nothing is known. It is generally regarded at the present time as an adsorption or surface solubility effect, to which we shall refer later. It has been shown—at least in some cases—that the ion is actually carried down with the coagulating colloid. Thus Linder and Picton (*Trans. Chem. Soc.*, **67**, 63, 1895) showed that when colloidal arsenic sulphide (negatively charged) was precipitated by $BaCl_2$ this salt was partly decomposed, a small quantity of $Ba(OH)_2$ being found in the precipitate, which could not be washed out completely, even after prolonged trial, and simultaneously a little free HCl was found in the supernatant liquid. This close union, which in the above instance exists, between the barium ion (in the form of baryta) and the coagulated colloid, is found frequently in the case of other ions in physiological liquids containing organic colloids. Reference has already been made to an analogous phenomenon in dealing with the osmotic pressure of certain physiological colloids and dyestuffs.

Coagulation of a colloid is in certain cases a reversible phenomenon. Besides being brought about by the addition of electrolytes, coagulation may also be caused by heating or cooling the colloidal solution as well as by electrolysis (more correctly speaking by cataphoresis), the particles being carried in virtue of their charges to one of the electrodes, where they become discharged and assume the gel form. Reversible coagulation is met with in the case of gelatin, when the coagulation has been brought about by temperature changes.

Reversibility will be further considered under the heading *Peptisation.*

It should be remembered that the colloidal state plays a greater *rôle* in ordinary chemical operations and reactions than is generally supposed. From the peculiar form in which substances (simple inorganic bodies) may be precipitated under certain conditions, it seems not unlikely that the colloidal state (sol and gel) represents at least a transition stage in such phenomena. Thus it is possible to precipitate barium sulphate (which is ordinarily a definitely crystalline substance) in a form not very different from a thin jelly, which passes over more or less rapidly into the stable form. This has already been referred to in connection with von Weimarn's work. Further, in the electrolytic precipitation of metals, such as copper, the formation of a smooth deposit is assisted by the presence of a little gelatin in the bath—an effect which reminds one of the "protective action" to be discussed subsequently. This effect in the case of copper electrolysis has, however, been called recently in question. The coagulation phenomena observed in the case of colloids has also been observed in the case of suspensions and emulsions, though these have been less extensively investigated (*cf.* Bodländer, *Jarhbuch für Mineralogie*, **2**, 147, 1893).

We are now in a position to return to the question of the electrical charge on a colloidal particle as determined by Burton (*l.c.*) from the amount of $Al_2(SO_4)_3$ just required to cause precipitation. Burton determined this by measuring the velocity of the colloid particle in an electric field when different amounts of electrolyte were present. The following data were obtained for colloidal silver in water :—

6·5 MILLIGRAMS SILVER PER 100 C.C. SOLUTION.

Grams of $Al^{\cdots}$[1] per 100 c.c. Solution.	Specific Conductivity of the Solution at 18° C.	Velocity of Silver Sol in cm. per Second under 1 volt per cm. Gradient.
0	$31{\cdot}0 \times 10^{-6}$	$22{\cdot}4 \times 10^{-5}$ towards anode
14×10^{-6}	$30{\cdot}3 \times 10^{-6}$	$7{\cdot}2 \times 10^{-5}$,, ,,
38×10^{-6}	$29{\cdot}7 \times 10^{-6}$	$5{\cdot}9 \times 10^{-5}$,, cathode
77×10^{-6}	$28{\cdot}5 \times 10^{-6}$	$13{\cdot}8 \times 10^{-5}$,, ,,

The colloid, which by itself is negatively charged, becomes eventually positively charged on addition of $Al_2(SO_4)_3$, and at the region in which the $Al^{\cdots}$ is 26×10^{-6} grams per 100 c.c. the velocity would be zero. This is called the *isoelectric point* (Hardy), and at this point the critical concentration of $Al^{\cdots}$ is reached for coagulation. As a matter of fact, the colloid which travelled towards the cathode was very unstable, and precipitated itself after a short time. The velocity method is the most exact method for determining the coagulating point, *i.e.* the "critical" amount of electrolyte required.

Burton in calculating the charge on the colloid assumed that the whole of the charged $Al^{\cdots}$ ions took part, and gave up their complete charge to the colloid. He found that the volume of each colloidal particle was 2×10^{-14} c.c., and since the mass of colloid is 6·5 milligrams in 100 c.c., the number of particles present—assuming the ordinary density for the silver, which is a little doubtful—he calculated to be 3×10^{10} per 100 c.c. Now 1 gram-ion $Al^{\cdots}$ carries $3 \times 96{,}550$ coulombs, that is, 26×10^{-6} grams $Al^{\cdots}$ carry 0·289 coulomb, and since this was required for 3×10^{10} particles, the charge (of opposite sign) carried by each colloid particle is $9{\cdot}6 \times 10^{-12}$ coulombs or approximately $2{\cdot}8 \times 10^{-2}$ electrostatic units. The result given by Stokes' expression is 8×10^{-8} electrostatic units, and that by the more chemically sound expression of Lamb is 8×10^{-5} electrostatic units. There is no doubt, therefore, that Burton's result is much too large. If we assume Burton's value for *e* and calculate the P.D. between the particle and the medium by means of the capacity expression, one finds V = 33 volts, which is of course quite impossible. For these reasons it has been suggested (Lewis, *Zeitsch. Koll.*, *l.c.*) that only a small fraction of the critical concentration of the $Al^{\cdot\cdot\cdot}$ ion is effective for coagulation. Lamb's expression yields the most trustworthy value—it is probably of the right order of magnitude. One other point requires to be mentioned, namely, that the charge on a colloid particle is several thousand times greater than that on a single electrolytic ion (*i.e.* if we assume the mass of one $Al^{\cdot\cdot\cdot}$ is of the order 10^{-23} grams, then this carries a charge of 3×10^{-9} electrostatic units, since 27 grams carry $3 \times 96{,}550$ coulombs). It is, therefore, impossible to assume with Billiter that one ion is a centre of condensation for several colloid particles.

---

[1] No allowance was made for hydrolysis of $Al_2(SO_4)_3$ giving rise to $Al(OH)_3$, which is very slightly dissociated.

It is also of importance to remember that at the isoelectric point the Brownian movement is believed to cease.

In connection with Burton's method of determining the charge, it has been assumed that the stability is a minimum just when the charge on the colloid is neutralised, that is when the P.D. between particle and medium is zero. Recent work of Powis (*Zeitsch. physik. Chem.*, **89**, 91, 179, 186, 1914) on an emulsion of a hydrocarbon oil in water indicates that there is a certain critical value of the contact potential, namely, ± 0·03 volt, and if by gradual addition of electrolyte the P.D. of the particle falls below this critical value, coagulation takes place, the coagulation being nearly independent of the P.D. when we are once below the critical limit. Measurements on colloidal arsenic sulphide gave similar results (Powis, *Trans. Chem. Soc.*, **109**, 734, 1916). This observation, especially if it be shown to be a general one, constitutes a considerable modification of Hardy's concept of the isoelectric point, and it is difficult to trace its possible mechanism.

The relative quantities of uni-, bi-, ter-, and quadri-valent cations required to produce rapid coagulation are much more nearly equal to the quantities required for the attainment of the critical P.D. value than to those which are required for the complete elimination of the P.D.

MECHANISM OF COAGULATION OF COLLOIDS BY IONS. CRITICISM OF THE HARDY-SCHULZE LAW.

It might possibly be inferred from what has been said in the preceding section about the coagulation of colloids by ions, that this effect is attributable solely to the existence of the opposite charge which neutralises the charge on the colloid. Whilst the fact of an ion being electrically charged certainly plays a part in the process, presumably by favouring, as a result of electrostatic attraction, the approach of the ion to the colloid, it must not be concluded that electric charge is the single condition for coagulation. It now appears that the process of preferential adsorption, presumably a capillary phenomenon, enters into the problem and is indeed the most important factor. By preferential adsorption we mean the adsorption, or condensation, or loose union of ions of one kind upon the colloid surface to the exclusion, partial or entire, of the other kind of ion. The relative coagulating power of a series of ions is governed rather by the relative adsorbability of the ions than by their electric charge. The effect is essentially specific, depending not only upon the ion but equally upon the nature of the colloid concerned. This point has been emphasised by W. D. Bancroft (compare *Journ. Phys. Chem.*, **19**, 363, 1915, or *Trans. Amer. Electrochem. Soc.*, **27**, 175, 1915), from whose paper a number of quotations will be made.

The Hardy-Schulze Law is a first approximation. "In case of doubt it is generally safe to assume that an ion of higher valence will be adsorbed more than one of lower valence; but it is a mistake to consider this so-called law as anything more than a guide. Since we are dealing with selective adsorption we shall expect to find that some univalent ions will be adsorbed by some substances more than some bivalent or trivalent ions."

"This is shown clearly in data by Oden on colloidal sulphur." A few of these data are given in the following table. In the second column are given the minimal quantities of the cation which can bring about coagulation, in the third column are given the reciprocals of these quantities, the so-called atomic precipitating power.

COAGULATION OF COLLOIDAL SULPHUR AT 18-20° C.

Salt.	Minimal Concentration in Gram-atoms of Cation per liter.	Atomic Precipitating Power of the Cation.
HCl . . .	6	0·16
LiCl . . .	0·913	1·1
NaCl . . .	0·153	6·1
Na_2SO_4 . . .	0·176	5·7
KCl . . .	0·021	47·5
K_2SO_4 . . .	0·025	39·7
RbCl . . .	0·016	63
CsCl . . .	0·009	108
$Mg(NO_3)_2$ . .	0·0080	125
$CaCl_2$ . . .	0·0041	245
$Ca(NO_3)_2$ . .	0·0040	247
$Sr(NO_3)_2$ . .	0·0025	385
$BaCl_2$ . . .	0·0021	475
$Ba(NO_3)_2$ . .	0·0022	461
$Cd(NO_3)_2$ . .	0·0493	20·3
$ZnSO_4$ . . .	0·0756	13·2
$Mn(NO_3)_2$ . .	0·0096	105
$AlCl_3$ . . .	0·0044	227
$Ni(NO_3)_2$ . .	0·0446	22·4
$CuSO_4$ . . .	0·0098	102

"Under the conditions of Oden's experiments, sulphur is a negative colloid and the precipitation is therefore due to an adsorption of cations. The first thing to notice is that the hydrogen ion is not adsorbed strongly by sulphur, the precipitating power of hydrochloric acid being much less than of lithium, sodium, potassium, rubidium or caesium chloride.

Instead of these univalent cations precipitating at the same concentration, the required concentration of lithium chloride is in round numbers one hundred times that of caesium chloride." The minimal concentration "values of barium and strontium are nearly equal, but calcium chloride requires a distinctly higher concentration. If we take the different bivalent ions the values range from 0·0756 for zinc to 0·0022 for barium, a ratio of over thirty to one. The univalent ion caesium has a greater precipitating power than the bivalent zinc, cadmium, nickel, and uranyl; and about the same precipitating power as the bivalent copper, manganese, and magnesium. The trivalent aluminium ion has about the same precipitating power as the bivalent calcium, and distinctly less precipitating power than bivalent strontium and barium. The specific nature of the adsorption comes out very clearly in the case of sulphur." Naturally the comparisons drawn above would be more strict if the same anion had been employed in every case. The conclusion, however, appears to be quite certain, *viz.* that the Hardy-Schulze Law is only true as a first approximation.

Bancroft points out that sulphur is rather an extreme case. Colloidal ferric hydroxide, as we have already seen, approximates much more nearly to the law. Other colloids, however, show a similar discrepancy to that met with in the case of sulphur, though to a less degree. Bancroft cites the following instances: colloidal platinum, silver, mastic, and albumin. (In connection with albumin see a paper by Bancroft, *Journ. Phys. Chem.*, **19**, 349, 1915.)

"Whilst there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions, and that the fundamental rule is that the adsorption is specific both as regards the adsorbing substance and the ion adsorbed."

PRECIPITATING ACTION OF ONE COLLOID UPON ANOTHER.

We have already seen that the favourable condition for bringing about coagulation of a colloid is the adsorption of an oppositely charged ion. If one colloid can adsorb another, then, if the charges are opposite in sign, it is to be expected that coagulation or precipitation of *both* will take place. Experiment has shown that positive and negative colloids will precipitate each other when in proper proportions and provided adsorption takes place (compare Bancroft, *Journ. Phys. Chem.*, **18**, 555, 1914). In dealing with the source of the charge on a colloid particle we have already seen that the charge is itself probably due to adsorbed ions. Hence when one colloid precipitates another it is the adsorbed ions which effect the coagulation.

In connection with this phenomenon, Bancroft (*Trans. Amer. Electrochem. Soc.*, *loc. cit.*) points out that "since complete neutralisation takes place only when one sol has adsorbed the amount of the sol carrying an *equivalent* amount of the ion having the opposite charge, it follows that the amount of one sol, necessary to precipitate a given amount of another sol, will vary with the degree of adsorption; it will therefore be a specific property and not an additive one. This can be tested experimentally on data by Biltz," given in the following table:—

1·4 mg. colloidal gold completely precipitated by

Colloidal	CeO_2.	Fe_2O_3.	ThO_2.	ZrO_2.	Cr_2O_3.	Al_2O_3.
	4	3	2·5	1·6	0·3	0·1-0·2 mg.

28 mg. colloidal Sb_2S_3 completely precipitated by

Colloidal	Fe_2O_3.	ThO_2.	CeO_2.	ZrO_2.	Cr_2O_3.	Al_2O_3.
	32	20	11	6·5	3·0	2·0 mg.

24 mg. colloidal As_2S_3 completely precipitated by

Colloidal	Fe_2O_3.	ThO_2.	CeO_2	ZrO_2.	Al_2O_3.	Cr_2O_3.
	13	6	4	2	2	0·5 mg.

"Alumina is more effective than [colloidal] chromic oxide in precipitating antimony sulphide and much less effective in precipitating arsenic sulphide. The alumina must therefore be adsorbed more by antimony sulphide than is chromic oxide, while the reverse must be true for arsenic sulphide. Cerium oxide is less effective than ferric oxide and thorium oxide in precipitating gold; but is more effective than either of these in precipitating the sulphides of antimony and arsenic. The phenomenon is thus specific varying with the nature of the two colloids."

"We can now take up the case of sols having the *same* charge. The statement that neither has any perceptible effect on the other is based solely on the fact that no precipitation occurs. We know, however, that cases of adsorption are not limited to colloids or electrolytes having opposite signs. Charcoal adsorbs both bases and acids. Silver bromide adsorbs silver ions or bromine ions as the case may be. There is therefore no theoretical reason why precipitated hydrated ferric oxide might not adsorb chromic oxide and *vice versâ.*"

Bancroft further considers the following interesting hypothetical case. "Suppose we have two sets of finely divided particles *neither* of which adsorbs the other appreciably, and let us also suppose that one set of particles adsorbs a given cation very strongly, while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well, but which will contain no free ions to speak of, because, by definition, the cations have been practically completely adsorbed by one set of particles, and the anions by the other set of particles. This particular case has not been realised; but an intermediate case seems to have been found by McBain and Martin (*Trans. Chem. Soc.*, **105**, 965, 1914) in sodium palmitate solutions," *i.e.* soap solutions.

From measurements of the electrical conductivity of such solutions McBain and Martin conclude that the conductivity is only to a very minor extent due to *free* hydroxyl ions. Further, on account of the fact that the rise of boiling point in certain soap solutions is practically all required to account for the sodium ions alone (McBain, *Trans. Faraday Soc.*, **9**, 90; *Kolloidzeitsch.*, **12**, 256, 1913), the conductivity cannot be ascribed to simple palmitate ions equal in number to the sodium ions. The suggestion made by McBain and Martin is that the conductivity is due in part to a colloidal anion possessing a mobility comparable with that of a true ion. McBain and Martin's investigations support the view that the undissociated soap, *i.e.* the undissociated sodium palmitate molecules, is present chiefly or entirely in the colloidal form.

As regards the phenomena here presented, Bancroft makes the following suggestion: "The sodium palmitate is hydrolysed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate, and possibly by the insoluble palmitic acid, though this seems less probable. The adsorbing substance thus becomes the anion owing to the adsorbed hydroxyl ions. The adsorption of an ion by a colloid gives us an electrically charged colloid, [or 'electrolytic colloid'], with a migration velocity of its own. This migration velocity, so far as it has been studied, is of the general order of magnitude of that of free ions (Zsigmondy, *Kolloidchemie*, **46**, 1912)."

PEPTISATION AND PROTECTIVE EFFECT.

Lottermoser and von Meyer (*Journ. f. prakt. Chem.*, **56**, 242, 1897) showed that egg albumin protected colloidal silver from becoming precipitated, and this observation has since been extended to numerous other cases by Zsigmondy, Paal, and others. Zsigmondy worked principally with colloidal solutions of gold, for which he found gelatin acted as an excellent preservative. In these cases one colloid stabilises another. In a particular experiment Zsigmondy used 10 c.c. of a gold-sol solution containing 0·05-0·06 gram per liter of gold. To this was added varying amounts of a protective colloid such as gelatin, and then 1 c.c. of a sodium chloride solution, density 1·07, approx. 2 normal, was added to the mixture. In this way Zsigmondy determined the minimal amount of the protective colloid which was required to just prevent the gold sol turning from red to blue, this being a definite stage in the act of coagulation of this colloidal metal. The amount of protective colloid required to effect this is known as the *gold number* of the protective colloid. This number has been measured in numerous cases, and serves as a convenient quantity wherewith to characterise the colloid in question.

To indicate the effectiveness of this protection it may be mentioned that a given gold solution was rendered stable even in the presence of sodium chloride, the concentration of which amounted to 0·2 equivalents per liter. If no protective colloid had been present the gold sol would have been turned from red to blue by sodium chloride at a concentration of 0·0002 equivalents per liter, and the gold completely precipitated by sodium chloride at a concentration of 0·002 equivalents per liter. In the following table are given the gold numbers of a few colloids:—

Colloid.	Gold Number.
Gelatin	0·005-0·01
Casein	0·01
Egg albumin	0·1-0·2
Potato starch	25

Paal (*Ber.*, 1902 and onwards) has investigated the protective effect of protalbic and lysalbic acids, both of which are colloidal. In this way a large number of metals, metallic oxides, and hydroxides, as well as certain salts, can be prepared, the resulting solutions being insensitive to electrolytes, heating or freezing.

A classic case of protection is met with in the formation of the Purple of Cassius, of interest for the production of ruby glass. In this, stannous chloride is allowed to act upon gold chloride in solution. The gold salt is thereby reduced to metal, and the stannic chloride so produced is hydrolysed into colloidal stannic acid which protects the finely divided gold and forms with it the purple.

Freundlich (*Kapillarchemie*, p. 455) discusses the possible mechanism of the protective effect without, however, coming to any very definite conclusion. Freundlich points out that the protective effect of a given colloid is not due to its own insensitivity to electrolytes, the most stable colloid being by no means the best protective colloid. Freundlich considers that the adsorption of the colloid to be protected by the protective colloid is the essential part of the process. The effect will therefore be specific, depending upon the nature of both.

In the phenomenon of *Peptisation* we have what might be regarded as the reverse of coagulation. That is, certain gels may be converted into sols by the action of reagents. Peptisation is defined by Bancroft (*Journ. Phys. Chem.*, **20**, 85, 1916) as consisting "in the disintegration of particles so that they form a colloidal solution". According to Bancroft we get "a permanent colloidal solution whenever the particles are small enough to be kept in suspension by their Brownian movements and in some way are kept from coalescing". Freundlich has assumed that all adsorption is accompanied by a lowering of the interfacial tension between the adsorbing material and the medium. "Any substance which is adsorbed by a second will lower the surface tension of the second substance and will therefore tend to disintegrate it, in other words to peptise it." Peptisation may therefore be expected to be brought about by a solvent, a dissolved non-electrolyte, an ion, a salt, and even by another colloid. Bancroft has therefore *identified protective effect with peptisation*, the protective effect of one colloid upon another being simply a special case of peptisation. The investigation of protective effect from this point of view has been carried out by Bancroft and his collaborators (compare *Journ. Phys. Chem.*, **19** onwards).

An interesting case of peptisation from the standpoint of analytical chemistry is met with in the action of excess caustic potash upon the hydroxides of zinc, aluminium, and chromium. These precipitates are gels, but dissolve in presence of excess alkali. Fischer and Hertz (*Zeitsch. anorg. Chem.*, **31**, 352, 1902) were the first to point out that chromium hydroxide can be peptised by alkali. Nagel (*Journ. Phys. Chem.*, **19**, 569) has confirmed this view, by experiments made on filtration through a collodion filter. With the peptised material inside the filtrate came through colourless, all the chromium being eventually left behind on the filter. In this process the hydroxyl ions which had kept the colloid in suspension were removed and the colloid precipitated itself. A solution of chromic chloride "dissolves" a certain amount of chromium hydroxide. Nagel (*loc. cit.*) by means of the collodion filter showed that this was likewise a case of peptisation. This idea of peptisation is of course very different from that held in such cases, according to which the solubility in alkali is due to the formation of a complex salt, more or less ionised. The case of zinc hydroxide is more complex than that of chromium hydroxide. Bancroft (*loc. cit.*) has found that "freshly precipitated zinc hydroxide is peptised by alkali; but the solution is very unstable, the zinc hydroxide often coagulating within half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate." As regards aluminium hydroxide the evidence (compare Slade, *Trans. Chem. Soc.*, **93**, 421, 1908) tends to show that peptisation is relatively unimportant, and that the true electrolyte sodium aluminate is formed. There may be conditions under which one form predominates, though nothing is known as regards this point.

Of course, quite apart from the question of peptisation, we are familiar with the fact that one and the same substance may exist in the colloid or in the crystalloid form (compare the investigations of von Weimarn). A similar behaviour has been observed in the case of aqueous solutions of bromophenanthrene-3-sulphonic acid when the concentration is changed (Sandqvist, *Kolloidzeitschr.*, **19**, 113, 1916). In dilute solution this substance acts as an ordinary electrolyte, but as the concentration increases colloidal behaviour manifests itself, and finally at great concentration the system functions as a crystalline liquid.

To return to peptisation. Bancroft, in the paper referred to, gives many other instances of peptisation. Thus we can obtain the effect by means of a solvent at high temperatures, though not at low. An instance of this is the solvent action of water upon glass. As an example of peptisation by a dissolved non-electrolyte we have the effect of sucrose on copper hydroxide. A particularly interesting case is met with in the peptising effect of a colloid which has already been peptised itself. We encounter this behaviour in the influence of chromium hydroxide upon ferric hydroxide. "Hydrous chromic oxide (*i.e.* hydroxide) is peptised by caustic potash, whilst hydrous ferric oxide (hydroxide) is not. If the chromium salt is present in large amount relatively to the iron salt, the ferric hydroxide will adsorb the peptised chromium hydroxide and be peptised by it, thereby going apparently into solution. If the ferric salt is present in excess, it will adsorb the peptised chromium hydroxide carrying it out of the liquid phase. It is to be noticed that the chromic hydroxide, when in excess, acts as a so-called protective colloid to the iron hydroxide." This is exactly analogous to the protective effect of gelatin upon colloidal gold.

To return to the classic investigation of Linder and Picton upon colloidal arsenic sulphide, it is important for our present purpose to point out that these authors found that the presence of excess hydrogen sulphide was essential to the stability of the colloid. As a matter of fact it is extremely difficult to remove all the hydrogen sulphide from arsenic sulphide. This is likewise a case of peptisation. Thus, Linder and Picton were able to disperse, *i.e.* peptise, coagulated sulphides by the action of excess H_2S. This point has recently been reinvestigated by Young and Goddard (*Journ. Phys. Chem.*, **21**, 1, 1917). By means of an ingenious piece of apparatus it has been shown that such sulphide colloids can be repeatedly precipitated and redissolved (peptised) by removing or adding H_2S. This result shows how erroneous is the statement that flocculation by electrolytes is an irreversible process. Provided the conditions are really reversed, the coagulation, certainly in the cases referred to, can be reversed too. It will be interesting to know if this is a perfectly general phenomenon. Young and Goddard also obtained evidence that H_2S protected colloidal zinc sulphide against the coagulating effect of potassium chloride.

EMULSIFICATION.

It will be convenient at this point to deal with a phenomenon which has much in common with the peptisation of colloids, namely, the preparation of stable emulsions. An emulsion consists of a finely divided liquid, such as a hydrocarbon oil, suspended in another liquid, the medium, water, for example. Reference has already been made to such systems. They differ chiefly from colloidal solutions in that the diameter of the particles or droplets is of the order 10^{-5} cm., whilst that of colloid particles is of the order 10^{-6} to 10^{-7} cm. The emulsions already discussed—in dealing with their electric charge—were extremely dilute. If a hydrocarbon oil be dispersed in pure water, only a very small mass of oil will form an emulsion, that is, will emulsify, excess oil floating on the top as a coherent layer. Through the introduction of emulsifying agents, however, very large quantities of oil may be suspended, such suspensions being apparently stable.

An emulsifying agent is essentially a substance which is capable of lowering the interfacial tension between the oil and the water. Soap is an example. It has been shown by experiment that soap lowers the tension of water against air. Further, the fact that soap gives rise to a foam is evidence of a lowering of surface tension, necessarily accompanied by adsorption of the soap in the surface layer (Gibbs' Principle, Vol. II., Chap. XI.), thereby rendering the soap film stable.

Alkali, *i.e.* hydroxyl ions, is stated to be a good emulsifying agent. Donnan (*Zeitsch. phys. Chem.*, **31**, 42, 1899) has investigated this effect and has shown that the efficiency of hydroxyl ions depends upon the possibility of soap formation *in situ*, in the interfacial layer. Thus with neutral olive oil the emulsifying power of alkali is small: with olive oil containing some free fatty acid, the emulsifying power of alkali is great, owing to the formation of the soap. Oleic acid itself was shown by Quincke to be emulsified with the greatest ease in alkaline solution, but not at all in pure water. Similar behaviour is exhibited by hydrocarbon oils, extensive emulsification occurring when free fatty acid was present as an impurity in the oil. Emulsification in such cases is due to the adsorption of the soap, which is itself a colloid. The process is therefore very analogous to the protective effect already discussed. Pickering (*Trans. Chem. Soc.*, **91**, 2012, 1907) has prepared emulsions of high oil content by emulsifying a hydrocarbon oil with various agents, albumin, glue, starch, and basic sulphates of iron and copper.

It seems probable that an emulsifying agent is essentially a colloid, adsorbable more or less strongly at the oil-water interface, such adsorption giving rise to relatively large aggregates of the emulsifier which, if present in sufficient quantity, may then give a kind of rigidity to the interface.

Thus Ramsden (*Proc. Roy. Soc.*, **72**, 156, 1903) obtained solid aggregates from the surface of all bubble-forming solutions by a simple sweeping-up process. The surface of many of these solutions was rigid, *i.e.* showed the properties of solid matter. There was a similar rigidity at the interface of many pairs of liquids capable of forming stable emulsions, and he concluded that the adsorbed material consisted of solid particles which stabilised bubble films and emulsion globules by acting as "taking-off" points for the liquid parts of the surface. The adsorbed material was assumed to be in contact with both phases.

Roon and Oesper (*Journ. Ind. Eng. Chem.*, **9**, 156, 1917) have emphasised the view, already held, that the efficiency of emulsifiers, especially in connection with pharmaceutical practice, depends not only upon the correct proportions of oil, water and emulsifier, but also upon the mode of preparation. In order to prepare an emulsion which may be diluted with water without losing stability, it is essential to mix the oil with the emulsifier in a limited quantity of water and afterwards dilute the system. If much water is employed to begin with, the emulsion cannot be obtained.

In view of the importance of (colloidal) soap for the process of emulsification, it is evident that the detergent or cleansing action of soap is likewise mainly due to the colloidal soap particle (and only slightly affected by hydroxyl ion as such). The soap, in fact, peptises the greasy dirt and removes it from the washed surface. If the dirt contains some free fatty acid, we would expect, of course, that alkali alone should be very efficient.

Besides emulsions of oil in water, that is, emulsions in which the oil is the disperse phase and water the continuous medium, many instances are known in which the reverse relations hold. It is a remarkable fact, for instance, that, using a sodium or potassium soap as an emulsifying agent, the resulting emulsion of oil and water is of the type in which oil is the dispersed phase and water the continuous. On the other hand, using calcium soap as the emulsifying agent, the resulting oil-water system consists of water droplets finely dispersed in a continuous oil medium.

Many ointments consist of an oil or fat containing water in a fine state of division. The same is true of mixed paints. This type of emulsion has been discussed by Bancroft (*cf. Journ. Phys. Chem.*, **17**, 501, 1913. This paper is one of a series in which the whole subject of emulsification is taken up in detail.)

Cream and butter are examples of two emulsions of opposite type, the cream consisting of droplets of fat suspended in water, the fat being stabilised by casein and other proteins. Butter, on the other hand, consists of fatty material as the continuous phase containing droplets of aqueous solution. The change in type produced by churning also corresponds to the changed physical properties.

In the case of margarine, it is usual to find an aqueous continuous phase, but the whole system seems ill-defined.

Various methods have been adopted to determine which type of emulsion obtains. Thus Clayton has suggested the use of electrical conductivity. If the continuous medium be oil, the conductivity is very low; if the continuous medium be water, the conductivity is high, owing to the ionised electrolytes present in the water.

A second method consists in the use of suitable staining agents, *i.e.* the use of dye-stuff which is insoluble in water but soluble in oil. Microscopic examination of the stained material is frequently employed to determine the type. This method, however, has the drawback that the introduction of the foreign dye-stuff may itself affect the emulsion.

Thirdly we have the Briggs' Drop method, which is very frequently employed. This depends upon diluting a drop of the emulsion with either water or oily solvent. If the original emulsion consists of oil droplets suspended in water, such a system will spread and distribute itself if further water be added, but will not distribute itself through oil. If, on the other hand, the original emulsion consists of water droplets suspended in oil, obviously further distribution will occur on the addition of an oily solvent but not on the addition of water.

We now turn to the problem of what determines *reversal of phase*, *i.e.* the change from one type of emulsion to another. That the type of emulsion is determined by the nature of the emulsifying agent was first recognised by Bancroft (*loc. cit.*), and the later work of Clowes, Newman, Briggs and Schlaepfer amply confirmed his conclusion. On Bancroft's view, the interface between two phases A and B is regarded as having two faces or sides. Let us imagine a plane interface of this kind. If the tension on one side, *i.e.* that of A, is lowered, that side will "give" and become *convex*. There will, therefore, be a tendency to form a sphere of the material B, this being the substance present at the side possessing the higher tension, that is, an emulsion of B in the continuous medium of A will be produced. Granted the existence of two phases differing in interfacial tension, the above conclusion is evidently correct. We have not yet, however, considered how such an effect, *or its equivalent*, might be brought about by the addition of what is now regarded as the essential constituent, namely the emulsifying agent itself. The earlier view was that the emulsifying agent had a different solubility in the two phases A and B. Since the emulsifying agent was assumed to lower the interfacial tension, it followed that the phase in which the emulsifying agent was readily soluble possessed a lower tension than the phase in which the emulsifying agent was relatively insoluble. The first of these phases would be the one whose tension would "give" most easily, and it would be the second phase that would be dispersed in the form of droplets. Let us take the specific case of oil and water and consider sodium, potassium and calcium soaps as emulsifying agents. The sodium and potassium soaps themselves disperse easily in water, *i.e.* possess a kind of solubility in water. Calcium soap, on the other hand, does not disperse in water but will disperse in oil. If some oil be shaken up with water, together with a small quantity of sodium or potassium soap, it is found that the resulting emulsion consists of oil droplets dispersed in the aqueous medium; the latter contains the soap. (The soap is adsorbed at the interface more or less strongly.) On the other hand, if calcium soap is the emulsifying agent, the reverse type of emulsion is obtained in agreement with the solubility relations referred to. The chief drawback to the above argument is the difficulty of really distinguishing two separate faces or sides at the interface, and also the vague and indefinite use of the term solubility.

In connection with the above, it should be mentioned that Pickering (*Journ. Chem. Soc.*, **91**, 2001, 1907) was the first to introduce "wetting' as a factor in emulsion equilibrium, a suggestion which has been accepted by later workers, but its function has always been very obscure, probably due to the lack of any precise definition of the term. It is to Ramsden (*Journ. Liv. Biol. Soc.*, **33**, 1919) that we owe the concept that *contact angle* is a fundamental factor in the problem. This is referred to below.

As already mentioned, Ramsden has emphasised the fact that the most efficient emulsifying agents are colloidal materials which produce (as a consequence of excessive adsorption) discrete particles which are lodged at the interface. It is well known that fine powders are in many cases good emulsifying agents. We infer, therefore, that the emulsifying function in such cases is due to the heterogeneous nature of the interface.

Instead of the vague term "solubility" of an emulsifying agent in a phase, Ramsden, in effect, ascribes the emulsifying action, and more particularly the type of resulting emulsion, to the degree of penetration of the emulsifying "solid" particles across the oil-water interface. Let us assume that the emulsifying particles are tiny spheres, small compared with the emulsion droplets themselves. In general, these solid spheres will lodge themselves at the oil-water interface with the greater part of the sphere immersed in one phase preferentially. The equilibrium position taken up will be determined, according to Ramsden, by the angle of contact which the emulsifying particle makes with the two liquid phases, oil and water.

As a working hypothesis, Ramsden suggests the following: When an insoluble solid is in contact with two immiscible liquids the liquid-liquid interface meets the solid at an angle which is characteristic of the three substances. In Fig. 51(*a*) the solid S is in contact with the two liquids W and O, where W represents water and O represents any other immiscible liquid. θ_{WO} is the contact angle measured on the water side of the interface.

It is now assumed that in an emulsion stabilised by insoluble solid particles, the liquid which forms the internal phase is the one on whose side of the liquid-liquid interface the contact angle is obtuse. In other words that the type of the emulsion is determined by the contact angle.

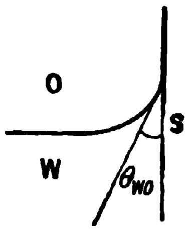


FIG. 51(*a*)

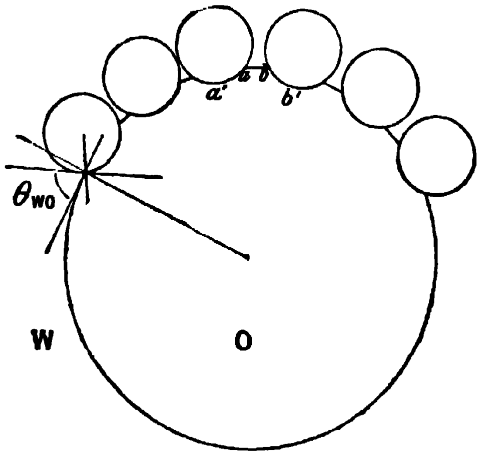


FIG. 51(*b*).

With the two liquids W and O, and the emulsifying solid S, when θ_{WO} is obtuse, the liquid W will be the internal or dispersed phase; when θ_{WO} is acute, as in Fig. 51(*a*), the liquid O will be the internal phase.

The equilibrium position of liquids with different solids must depend on the different ranges and magnitudes of the intermolecular forces between the liquid and the solid. *The stronger the attraction between solid and liquid, the greater will be the tendency for them to acquire the maximum possible common area of contact.* We should expect therefore, that a solid which has an acute angle of contact with a liquid would attract the liquid more powerfully than a solid which has an obtuse angle.

Fig. 51(*b*) indicates how the type of emulsion depends on the magnitude of the angle of contact, *i.e.* whether acute or obtuse. The magnitude of the angle obviously determines the degree of penetration of the tiny spheres of emulsifier into each phase.

In the figure, the angle of contact θ_{WO} is acute. This may be interpreted to mean that the energy which is set free in the liquid W when S comes into contact with W is greater than the energy which is set free when S comes into contact with O and consequently the penetration of S across the interface is as shown. (This unequal penetration is the analogue of the older view of greater "solubility" of the emulsifier in W than in O.) With the conditions as illustrated by Fig. 51(*b*), we have still to see, however, why the O phase is the internal or dispersed one.

Consider a segment of the O-W interface between any two points a and b. This interface tends to contract. Let us postulate in the first place that there are sufficient particles of S to make a layer in which each S particle touches its neighbour at the equatorial point. Under these conditions the tension between a and b will tend to rotate two contiguous S particles so as to approximate their internal "poles" a' and b', with the consequence that the interface stretching between a and b will be distorted and become concave with respect to O (as shown). On the other hand, if the S spheres had projected more into O than into W, the positive tension between a and b would have caused curvature of the interface in the opposite sense and W would have become the internal phase. In this manner the type of emulsion is shown to depend on the nature of the emulsifying agent.

It must be emphasised, however, that in the above set of conditions the curvature of the interface (*i.e.* the type of emulsion) is brought about by the positive tension between a and b operating when the S particles were so densely adsorbed that they touched at their equatorial lines. This touching is the equivalent of repulsion; owing to this repulsion the S spheres cannot approximate more closely and the tension between a and b produces the curvature.

There is evidence, however (*i.e.* absence of solidity of the surface film, *cf.* Ramsden, *loc. cit.*), that the emulsifying agent is not always packed in the above manner. Emulsification can be brought about even when the emulsifying particles S are separated from one another. In this case we have still an effective repulsion acting between neighbouring S particles, this repulsion being substituted for the actual contact in the case already considered. Granted that such a repulsion really does operate we would possess a satisfactory theory of emulsification.

According to Ramsden an effective repulsion between neighbouring S particles may be anticipated under certain conditions which are determined by interfacial or surface tension considerations. Let us return to the equilibrium conditions represented by Fig. 51(*a*) and let us suppose, for the sake of simplicity, that the phase O consists of air. (The conclusions we arrive at will have significance in the first place for foams, *i.e.* emulsions of air bubbles in liquids.) The capillarity equation which defines the equilibrium position of the three phases, air, water, and solid, at their common point of contact is

$$T_{W\circledS} + T_{WO}\cos\theta_{WO} = T_{O\circledS}$$

when T_{WO} denotes the ordinary surface tension of the liquid W in contact with air (O), $T_{W\textcircled{S}}$ the tension in the W layer contiguous to the solid, *i.e.* the tension in this layer under the influence of the solid, and $T_{O\textcircled{S}}$ is the tension in the air layer contiguous to the solid and under the influence of the solid. It follows that

$$\cos \theta_{WO} = \frac{T_{O\textcircled{S}} - T_{W\textcircled{S}}}{T_{WO}}.$$

The tension in the air represented by $T_{O\textcircled{S}}$ is in general small compared with the other tensions named so that we can write for this case

$$\cos \theta_{WO} = \frac{- T_{W\textcircled{S}}}{T_{WO}}.$$

In the case considered, *i.e.* when W wets the solid S, the angle θ_{WO} is acute. Hence its cosine is a positive quantity. The tension T_{WO} is likewise positive, hence $T_{W\textcircled{S}}$ is a negative tension, *i.e.* $T_{W\textcircled{S}}$ denotes an expansile force in contradistinction to T_{WO} which is contractile.

Let us return to Fig. 51(*b*) and consider the conditions obtaining in a layer of W between two neighbouring S particles, *i.e.* in a direction at right angles to the surface of the oil droplet itself. (It will be recalled that the orientation of the S particles relative to the droplet O is dependent ultimately on the fact that θ_{WO} is acute.) In the layer of water separating two solid particles of the above nature, the tension in the water layer contiguous to each solid is (as shown above) expansile. This expansility is the same all round any one S particle in so far as it is immersed in the liquid considered, *i.e.* W. The expansile effect exists throughout a layer comparable with the accepted range of molecular attraction, *i.e.* 10^{-7} cm. As long as neighbouring S particles are further apart than this they do not influence one another. If, however, they approach to within this range—even though they do not touch and the layer is consequently mobile—the expansile tension may be affected, for quite evidently the expansility in the layer of liquid near to the solid (which it wets) has its origin in a mutual influence of the solid itself upon the contiguous liquid. In fact, the magnitude, and even the sign of any interfacial tension is dependent on the difference between two cohesions which we may denote by K_{SW} and K_{WW} respectively, where K_{SW} denotes the attraction of S for W and K_{WW} denotes the mutual attraction of the molecules of W, measured in both cases per unit cross-sectional area. The cohesion may be regarded as operating at right angles to the interface. For the case in question we have, according to Ramsden,

$$T_{W\textcircled{S}} \propto K_{WW} - K_{WS}.$$

For a layer of water greater than the range of molecular attraction, K_{WW} has a value characteristic of water in bulk. If, however, the distance apart of the two spheres of S is less than this, the value to be attached to K_{WW} has to be modified in the sense that it approaches more nearly to K_{WS} itself. Now in the conditions considered, T_{WS} is expansile, *i.e.* negative, and therefore $K_{WW} < K_{WS}$. Consequently the effect of the approximation of the two spheres of S is to raise the value to be ascribed to K_{WW} and consequently to *diminish* the value of the expansile force of $T_{W\textcircled{S}}$. This is what occurs *between* the two spheres. The value of $T_{W\textcircled{S}}$, however, contiguous to other regions of two neighbouring spheres—the portions most remote from the O droplet—retains its original value, which is now greater than the diminished expansility of the water layer between the two S spheres. The result of this is that water is forced in between the S spheres which are thus effectively repelled from one another without being actually in contact. The conditions represented by Fig. 51(*b*) can therefore be realised and an emulsion of a type defined by θ_{WO} obtained.

Smoluchowski's Theory of the Rate of Coagulation of a Colloid Sol.

Smoluchowski[1] was led to the theoretical treatment of the problem of coagulation from a consideration of certain experiments of Zsigmondy on colloidal gold. Zsigmondy found that, on coagulating a gold sol by means of electrolyte, the speed of coagulation increased with increasing electrolyte concentration until a maximum speed was obtained. This maximum speed is independent of all further increase in electrolyte concentration. This fact formed the basis of Smoluchowski's theory of "rapid coagulation".

In the absence of electrolyte, the electrical double layer on the particles prevents coalescence taking place on impact of one or more particles. Addition of electrolyte to the colloid system diminishes the electrical double layer on the particles, and a force of attraction comes into play. The region of "rapid coagulation," as formulated by Smoluchowski, corresponds to a state of complete electrical discharge of the particles and consequently of maximum attractive forces between them.

According to this theory each particle in a homogeneous sol is supposed to possess a sphere of attraction R, within which the attraction is so strong that any other particle, whose centre enters this sphere, is firmly held.

In an originally uniform sol, whose particles have been completely discharged, the initial number of particles whose centres are less than R apart is vanishingly small.

---

[1] Smoluchowski, *Zeitschr. physikal Chem.*, 92, 129, 1917.

In course of time, Brownian movement brings the particles into all possible configurations. In consequence of Brownian movement and of the existence of "spheres of attraction" an irreversible state of coagulation is finally set up. It would be futile to merely give the deduction of Smoluchowski's equation; that will be found in the original paper.

Smoluchowski, combining probability considerations and the laws of diffusion, derives a series of equations which give the rate of disappearance of the particles in a colloid solution during "rapid" coagulation. The following equation gives the rate of disappearance of primary particles:—

$$\nu_1 = \frac{\nu_0}{(1 + \beta t)^2}$$

where ν_0 is the number of primaries at zero time, ν_1 is the number of primaries at a time t, and β is a constant equivalent to $4\pi \mathrm{DR}\nu_0$, where D is the diffusion coefficient and R is the radius of the sphere of attraction.

Smoluchowski has also attempted to extend his theory to *slow* coagulation. In this case owing to incomplete discharge of the electric layers, the attractive forces between the particles are not at their maximum and hence only a fraction of the collisions result in union. A probability factor ϵ is therefore introduced to allow for this. The resulting equations obtained by Smoluchowski are identical in form with those obtained for rapid coagulation except that the term β is now replaced by $\epsilon\beta$. Thus the equation $\nu_1 = \frac{\nu_0}{(1 + \beta t)^2}$ becomes $\nu_1 = \frac{\nu_0}{(1 + \epsilon\beta t)^2}$. The probability factor ϵ is assumed by Smoluchowski to be constant throughout the course of coagulation.

A fundamental assumption of Smoluchowski's theory is that the rate of disappearance of primaries is greater than that of a simple "bimolecular" reaction. As a corrollary to the above it would follow that if coagulation were treated as a bimolecular process, the bimolecular velocity "constant" k_{bi} should *always* increase with time for both slow and rapid coagulation. In the case of slow coagulation, however, a rapid fall in the Smoluchowski constant and also in k_{bi} is obtained experimentally, although theoretically the former should remain constant and the latter should rise.

Smoluchowski's equations have been tested by Zsigmondy,[1] by Westgren and Reitstötter,[2] by Kruyt and Arkel,[3] by Mukherjee and Papaconstantinou,[4] and by Anderson.[5]

---

[1] Zsigmondy, *Zeitschr. physikal Chem.*, **92**, 600, 1917.
[2] Westgren and Reitstötter, *ibid.*, **92**, 750, 1917.
[3] Kruyt and Arkel, *Rec. Trav. Chim. Pays Bas.*, **39**, 656, 1920.
[4] Mukherjee and Papaconstantinou, *Phil. Mag.*, **44**, 305, 1922.
[5] Anderson, *Trans. Faraday Soc.*, **19**, 623, 1924.

The act of coagulation of colloidal gold involves a change of colour from red to blue. The red is supposed to be due to primary particles. On the assumption that the percentage of red remaining is proportional to the change in the absorption coefficient, the values of β can be calculated.

In addition to the above investigations, attention must be drawn to those of Hatschek,[1] who devised a colorimetric method of testing the applicability of Smoluchowski's equation. The principle of the method is as follows: A rectangular cell divided by an oblique partition contains, in one half, red gold sol and in the other half, blue sol in suspension stabilised by gelatin. This cell when viewed from the front shows a colour range varying from 100 per cent. red to 100 per cent. blue. A second cell, similar to the first, is placed on top and into it is poured the coagulating sol which is being examined. The colour of the sol in the upper cell varies gradually, with time, from 100 per cent. red to blue. By direct comparison of the tints in the upper and lower cells, the percentage of red remaining at any instant can be estimated directly. Hatschek's method has been employed by Anderson. A few of the results thus obtained are cited below.

The experiments indicate that for the coagulation of gold sols, by means of electrolytes, there is a "rapid" region in which Smoluchowski's equation holds reasonably well. In a region of smaller electrolyte concentration than the above, an excessive slowing down in the speed of coagulation with time is observed. The general conclusion arrived at is that the Smoluchowski equation is strictly limited in its application.

Conditions Approximating to Rapid Coagulation.

Electrolyte—Barium Chloride.

Gold Sol 22—$BaCl_2$ = 0·00332 N. Gold Sol 19—$BaCl_2$ = 0·00166 N.

Time (Secs.).	Per Cent. Red.	β.	Time (Secs.).	Per Cent. Red.	β.
0	100·0	—	0	100·0	—
15	46·6	1·860	20	53·3	1·11
25	33·3	1·760	40	38·6	0·915
45	20·0	1·650	55	29·3	0·925
80	9·3	1·710	80	24·0	0·777
130	4·3	1·850	115	16·0	0·782
			150	10·6	0·828
			190	6·6	0·913

The constancy of β in the above table is good. The results may be taken as indicating that the Smoluchowski equation is holding in the region observed.

---

[1] Hatschek, *Trans. Faraday Soc.*, 17, 499, 1921.

SLOW COAGULATION.

Electrolyte—Barium Chloride.

Sol 19—$BaCl_2$ = 0·001 N.

Time (Minutes).	Per Cent. Red.	β.	$k_{bi} \times 10^3$.
0	100·0	—	—
1	86·7	0·074	1·53
2·33	73·3	0·071	1·58
3·75	66·6	0·060	0·96
5·66	60·0	0·051	0·86
24·50	46·6	0·018	0·20
36·0	33·3	0·020	0·74
67·5	28·0	0·013	0·18
107·00	17·3	0·008	0·056

It will be seen in the above that β and even k_{bi} fall rapidly—the more so the slower the speed of coagulation. In addition to a fall in β, it is possible to arrange the electrolyte concentration so that the sol never reaches 100 per cent. blue after standing many hours.

Smoluchowski asserts that the curves depicting slow and rapid coagulation should have a similar form, the only varying factor being the probability that an impact will give union. For so-called "rapid" coagulation this probability factor is unity and for non-rapid coagulation it is ϵ, where $\epsilon < 1$. This factor ϵ is assumed by Smoluchowski to be constant throughout the course of any one coagulation, but this is not found to be the case. The factor ϵ depends upon, and must be some function of, the residual nett charge on the particle. When two charged particles unite, the surface density of the charge on the complex is different from that on the original particle and therefore different repulsive forces come into play. It is therefore very probable that the factor ϵ for union between a charged primary and a charged complex, is less than the factor ϵ for union between two primaries.

It is thus evident that the probability factor is varying continuously as the complexes become larger. The falling value of ϵ would partly account for the falling value of β observed in this region, since the β calculated in the previous tables implicitly contains ϵ. However, even if this modification were introduced into the Smoluchowski equation, the rate of disappearance of primaries would, theoretically, always be greater than that obtained by a bimolecular process, assuming primaries simply united with each other. The data obtained, however, show that in some cases the value of k_{bi} falls, *i.e.* coagulation is proceeding even more slowly than would be expected on the basis of a bimolecular process. Furthermore, if primaries did disappear simply by union with each other it would follow that once coagulation has commenced it should proceed until no more primaries are left. On this basis incomplete colour change from red to blue should not be possible, since any red colour remaining would indicate unchanged primaries (attributing the red colour to the latter). However, incomplete colour change does occur and simply depends upon the concentration of the electrolyte present. This phenomenon admits of two explanations:—

1. It may be due to the possibility that the rate of disappearance of primaries is counterbalanced by an opposing effect: that is, primaries are being reformed either by spontaneous disruption of complexes or by collision of complexes with each other. Such reversibility however would seem to entail a behaviour, on dialysis, of incompletely coagulated sol which has not yet been observed.

2. A more probable explanation would seem to be that the initial primary particles (giving the red colour) are *unequally* charged. In the case of slow and eventually incomplete coagulation very small amounts of electrolyte are used and it is conceivable that the amount adsorbed is not sufficient to reduce the charge of some of the particles (which initially carry an excessive charge) below the critical limit which will permit coagulation to take place.

If this conception of unequal charge is correct, the Smoluchowski equation could not be expected to be applicable in general.

In reviewing the whole problem of coagulation, it would appear that the Smoluchowski equation in its present form is limited in its application. Before it can be applied to all types of coagulation it apparently requires modification to allow for the two factors:—

(*a*) The decrease of the probability factor as coagulation proceeds.
(*b*) The existence of incomplete coagulation as a consequence of unequal, and in some cases therefore, of excessive initial electrical charge on the primary particles.

GELS. THE IMBIBITION OR SWELLING OF GELS.

The gels, or flocculated forms of colloidal substances, are regarded as two-phase systems, consisting of a fine network of colloidal material which encloses some of the medium and part of the precipitant (compare Whitney's experiments on the precipitation of arsenic sulphide by barium chloride). In some cases the gel is semi-solid, granular, as in the case of silicic acid and metallic oxides. In others the gel is elastic as in the case of gelatin or agar-agar. In the latter cases we encounter the phenomenon of swelling or imbibition through the absorption of varying quantities of the liquid medium. This phenomenon is of importance in physiology and pathology,[1] and technically as in tanning. If the gel of gelatin or agar-agar is dried, it contracts, without, however, exhibiting any of the gaseous spaces such as occur in the case of dried silicic acid. If the dried material be brought into contact with water, the mass swells up until a maximum is reached at the end of some hours or even days. It is noteworthy that whilst there is a marked increase in volume of the colloid itself, at the same time the whole system, water + colloid, actually decreases in volume as a result of the process. In the case of the gel of Laminaria (algæ) the force exerted in the swelling has been measured, by determining the pressure P which must be applied in order to express a little of the water. Considerable pressure is required, its magnitude being a function of the true colloid content of the swollen mass. The following values have been obtained:—

---

[1] E. Pribram, *Kolloidchemie Beihefte*, Bd. II.

Weight per cent. of Dry Colloid.	P in atmos. including that of the Air itself.
25	3
42	17
57	41

The magnitude of the imbibition force has also been demonstrated qualitatively in the drying process. If gelatin be dried on a glass plate it has been found that the plate becomes doubly refracting, indicating distortion, and in an extreme case the plate may be bent and broken.

Imbibition is affected by the presence of electrolytes in the liquid medium with which the colloid gel is in contact. In the case of gelatin gel it has been found that in presence of the chlorides of potassium, sodium, and ammonium, the nitrate and bromide of sodium water is taken up more quickly by the gel than in pure water itself; whilst in presence of sodium sulphate, citrate, tartrate, and acetate the imbibition proceeds more slowly than in pure water. The thiocyanate ion is remarkable for its accelerating influence on the process. On the other hand, substances which contain the hydroxyl group, such as alcohol or sucrose, inhibit the swelling. Freundlich (*loc. cit.*) regards the effect of the ions as an instance of selective adsorption. It has already been mentioned that it is extremely difficult to wash out completely the last traces of salts from certain physiological colloid materials. Their presence, due to adsorption, probably plays a part in the imbibition exhibited by these substances.

ELECTRICAL OSMOSE OR ENDOSMOSE.

As already mentioned endosmose denotes the movement of a liquid along a capillary tube or through a membrane—which consists of a large number of more or less parallel capillary tubes—when a difference of potential is exerted along the tube. It has long been known that if water be placed in a vessel divided in half by a vertical porous membrane and an electrode be placed in each half, then the water will move through the membrane under the influence of the external E.M.F. applied at the electrodes, so that the water level rises in one compartment and falls in the other. The phenomenon is analogous to cataphoresis, with this difference, however, that in cataphoresis the liquid medium remains approximately stationary, during the passage of the suspended particles through it, whilst in endosmose the medium itself moves, the diaphragm being fixed.

The purely physical aspects of the phenomenon, *viz.* the relation between the difference of hydrostatic pressure and the applied E.M.F., the amount of liquid transported in unit time and the current strength, etc., are clearly summarised by T. R. Briggs (*Journ. Phys. Chem.*, **21**, 198, 1917).

Endosmose has been investigated by Perrin (*Journ. Chim. phys.*, **2**, 601, 1904). The important generalisation made by him is: porous membranes become positively charged in a solution containing acid, *i.e.* hydrogen ions, whilst they become negatively charged in a solution containing considerable quantities of hydroxyl ions. Hence if an acid solution be employed and an external p.d. applied, the solution will travel from the cathode to the anode chamber, because the solution is negatively charged with respect to the membrane, and therefore the membrane tends to be driven to the cathode whilst the solution actually does move towards the positive pole, the anode. If the solution be alkaline, it will travel in the reverse direction, namely, from anode to cathode. According to the nature and concentration and absorbability of the various ions it seems possible to give to a diaphragm almost any kind and extent of a charge we please. A neutral membrane can thus be prepared, and as a matter of fact specific membranes have already been employed on the technical scale for the preparation, purification and isolation of numerous substances. This will be referred to briefly in the section on technical applications of colloid chemistry.

Although Perrin's generalisation is an extremely useful guide to endosmotic behaviour in general, it can scarcely be taken as covering the whole phenomenon. Thus Perrin himself found that both acid and alkali flowed to the cathode through a plug of cotton wool. The cotton wool was therefore negatively charged. As the strength of the acid was increased, however, a point was finally reached at which the flow ceased. This we take to be the iso-electric point, there being now no effective difference of potential between the membrane and the solution. Glass diaphragms behaved similarly to the cotton wool diaphragm in being negatively charged as a rule, whilst barium carbonate and to a less extent chromic chloride tended to take on a positive charge.

Freundlich (*Kapillarchemie*) was the first to point out that endosmotic effects of various solutions were a question of selective or preferential adsorption of a given ion. In acid solution the membrane is in general positive because of the adsorption of hydrogen ions; in alkaline solution the membrane is generally negative because of the adsorption of hydroxyl ions. Bancroft has recently used this idea in connection with certain apparent exceptions to Perrin's generalisation which he shows are only apparent and not real (compare *Trans. Amer. Electrochem. Soc.*, **21**, 233, 1912).

"If we take an acidified copper sulphate solution and a porous cup we find that electrical endosmose carries the solution through the walls of the cup from anode to cathode, which is not the direction that Perrin's law would lead us to expect—[the solution being acid]. On the other hand the solution passes to the anode if we substitute copper nitrate and nitric acid for the corresponding sulphates. The sign of the charge on a diaphragm depends on the relative adsorption of cation and anion, being positive if the cation is adsorbed to a greater extent than the anion, and negative if the reverse is the case. Let us assume that for equal concentrations, hydrogen as ion is adsorbed somewhat more readily than sulphate as ion, while copper as ion and nitrate as ion are only adsorbed to a relatively slight extent. [That is, the relative adsorbability of the ions is according to the series, $H^{\cdot}>SO_4''>Cu^{\cdot\cdot}>NO_3'$.] In that case the diaphragm will be charged positively in sulphuric acid and in nitric acid; but will be charged negatively in [neutral] copper sulphate. Electrical endosmose will then carry sulphuric and nitric acid solutions to the anode and a copper sulphate solution to the cathode, which is what happens. An acidified copper nitrate solution will also move to the anode because hydrogen as ion will be the deciding factor. The situation is different with an acidified copper sulphate solution, especially if the concentration of copper sulphate is high and that of sulphuric acid is low. Since the adsorption of sulphate as ion increases with increasing concentration, there will come a point at which sulphate as ion is adsorbed more strongly than hydrogen as ion. The charge on the diaphragm will then reverse—[from positive to negative]—and electrical endosmose will carry the solution through the diaphragm from the anode to the cathode, which is what happens experimentally."

The present position regarding the mechanism of endosmose is summed up by Briggs (*loc. cit.*), from whose paper the following quotation is made:—

"We postulate that every solid has a specific adsorbing power for a given ion, which depends upon the specific surface of the solid [compare Wo. Ostwald, *Grundriss der Kolloidchemie*, p. 29], upon the temperature, upon the concentration of the particular ion in the solution, and upon the other ions present, or adsorbed previously by the solid. When the ion content of a liquid is vanishingly small, we shall have but little ion adsorption and little electrical endosmose. Non-dissociated and non-dissociating liquids show little electrical endosmose (Perrin, Coehn), an experimental confirmation of the preceding statement. On the other hand 'pure' water shows marked endosmose through many solids. This is a case of preferential ion adsorption where the ions are produced both from the ionisation of water itself and the solution of the solid which is a very important matter in some cases (notably glass). Now, since the majority of solids are negative against water, we postulate that hydroxyl ions are usually adsorbed in preference to hydrogen ions. Freshly precipitated alumina is reported to be electro-positive; my [Briggs'] idea regarding this is not that alumina on dissolving sends out rapidly diffusing hydroxyl ions and becomes positive against the solution, but that it adsorbs aluminium or hydrogen ions more easily than hydroxyl ions. Crystalline alumina in the form of alundum is electronegative against water, and in this respect shows a distinct difference as compared with the gelatinous form, a difference which may be due, not only to the alteration of its surface by agglomeration, but also to its slower rate of solution. In discussing the potential of a solid against water *originally pure*, we must accordingly take two factors into account:—

"1. The specific adsorption capacity of the solid for hydrogen and hydroxyl ions produced by the dissociation of the water.

"2. The solution of the solid, which though extremely small in many cases, may produce ions that are strongly adsorbed.

"Hydrogen ions are often adsorbed preferentially from solutions containing them, especially from acids, though the rule is by no means a general one. My [Briggs'] experiments have shown that alumina, which is positive in dilute hydrochloric acid, is weakly negative in citric acid, where the equivalent selective adsorption of the citrate ion must be greater than that of the hydrogen ion. Moreover, we know that metal sulphides are peptised by hydrogen sulphide, an acid, yet the adsorbed ion is sulphur and not hydrogen; the particles in suspension are electro-negative [*cf.* Linder and Picton, *loc. cit.*].

"In general the same statement applies to the adsorption of hydroxyl ions. Solids seem to have a somewhat greater adsorption affinity for hydroxyl ions than for hydrogen ions, though there are notable exceptions to this generalisation."

The account which has been given of the mechanism of coagulation of colloids by ions, the precipitating action of one colloid upon another, the phenomenon of peptisation (of which protective effect is a particular case), emulsification of oils, the phenomenon of imbibition of gels, and finally endosmose of solutions through solids, will serve to emphasise the fundamental significance of selective or preferential adsorption for all these processes. A definite stage has been reached in our knowledge of such phenomena. The next advance will be the elucidation of the nature and cause of this selective action. About this very little is known.

The problem of the structure of membranes in general will be taken up in Chap. VIII., Vol. II., in connection with the mechanism of osmotic pressure of solutions.

VISCOSITY OF COLLOIDAL SOLUTIONS.[1]

The concentration of many colloidal solutions, such as those containing metals and sulphides, is very small. Thus colloidal solutions of metals contain approximately 0·05 to 0·1 per cent. of metal, colloidal arsenic sulphide approximately 3 to 4 per cent. of sulphide. The viscosity of dilute solutions naturally differs only slightly from that of water itself. The case is different with organic colloids, such as gelatin, albumin, etc., as well as with colloids such as silicic acid, alumina, etc.

---

[1] [A survey of the subject of viscosity up to 1913 will be found in *Trans. Faraday Soc.*, 1913. A later review (up to 1917) is given by E. Hatschek in the Report of the Committee on Colloid Chemistry and its Industrial Applications (Brit. Assoc. Report, 1917).]

The following table indicates the increase in viscosity with concentration in the case of silicic acid sol at 20° C.:—

Concentration of Silicic Acid.	Viscosity of Solution.
0·0 (pure water)	0·012
0·81 per cent.	0·012
1·96 "	0·032
3·67 "	0·165

Einstein (*Ann. Physik.*, **19**, 289, 1906) deduced the following expression for the viscosity of a colloidal solution:—

$$\eta = \eta_0 (1 + \phi)$$

where η is the viscosity of the colloid, η_0 that of the pure medium, and ϕ the volume of colloidal matter present per unit volume of the medium. Later Einstein modified his expression, which took the form—

$$\eta = \eta_0 (1 + 2{\cdot}5\, \phi).$$

This formula is based on a number of assumptions which necessarily restrict its applicability: (1) the particles are regarded as rigid spheres; (2) the radius of the particle is large compared with the range of sensible molecular attraction; (3) the value of ϕ must not be too large, *i.e.* the concentration of the solution must not be high.

Hatschek has developed a similar formula (*Kolloid-Zeitschrift*, **7**, 310, 1910; *ib.*, **8**, 34, 1911) in which the numerical factor is 4·5.

Experiment has shown, in the first place, that the numerical value of the factor (2·5 in Einstein's expression, 4·5 in Hatschek's) is not really a constant, but varies with the nature of the system, values ranging from 1·5 to 4·75 having been obtained (*cf.* Freundlich and Ishizaka, *Trans. Faraday Soc.*, **9**, 66, 1913; W. Harrison, *Journ. Soc. Dyers Colour.*, **27**, April, 1911; Bancelin, *Kolloid-Zeitschrift*, **9**, 154, 1911; Miss Humphrey and Hatschek, *Proc. Phys. Soc. Lond.*, **28**, Part V., 274, 1916). In addition to the variation in the factor, it has been found that a simple linear relation does not reproduce the observations with sufficient accuracy in any single case. The problem of accounting for the viscosity of colloidal solutions is therefore still unsolved. Smoluchowski has dealt recently with the difficulties of finding an expression universally applicable (*Kolloid-Zeitschrift*, **18**, 190, 1916). It is known, for example, that coagulation is usually accompanied by an increase in viscosity, a fact which is considered to be at variance with the Einstein formula. Smoluchowski (*loc. cit.*) has shown that, even if the particles remain approximately spherical on coagulation, the total volume of the coagulated material must be at least $3\sqrt{2/\pi} = 1{\cdot}35$ times as large as that of the uncoagulated material, and hence, for the same mass of colloid, coagulation may be expected to lead to an increase in viscosity.

Smoluchowski has further arrived at the very important result that the electric charge on the particles effectively increases the viscosity.

The actual experimental method of measuring the viscosity is an important matter. This is particularly the case with those systems which form semi-solid layers at a surface of phase discontinuity. The constitution of such layers is briefly considered in Vol. II., Chap XI.

THE VISCOSITY OF COLLOIDAL SOAP SOLUTIONS CONTAINING ELECTROLYTES.

In this connection reference may be made to a paper by F. D. Farrow (*Trans. Chem. Soc.*, **101**, 347, 1912), who examined the viscosity of solutions of sodium palmitate (soap) in water in presence of varying amounts of electrolytes such as NaOH, NaCl, KCl. Sodium palmitate is partially hydrolysed, and the products of hydrolysis have been shown to exist to a certain extent in the colloidal form. The material forming the colloidal particles is known as the "disperse phase," the medium in which the particles are suspended, as the "continuous phase". The viscosity curves obtained were similar in all cases, as is shown by the diagram (Fig. 52), which illustrates the effect of varying concentration of electrolyte upon the viscosity of constant mass of sodium palmitate. The lowest curve refers to addition of KCl, the middle curve to NaOH, and the uppermost to NaCl. On addition of electrolyte to a freshly prepared solution of sodium palmitate, a fall in the viscosity was observed, *i.e.* the viscosity tended in the direction of the value for pure water. On further addition of the electrolyte the viscosity increased. Woudstra (*Kolloid-Zeitsch.*, **8**, 73, 1911) observed a similar behaviour in the case of colloidal ferric hydroxide. The sodium palmitate solution is heterogeneous, the disperse phase containing a much higher ratio of alkali and fatty acid to water than is the case in the relatively much more dilute and continuous "water phase". According to Farrow, one may regard the disperse phase as bounded by a semi-permeable membrane across which equilibrium is set up by the various constituents. On adding an

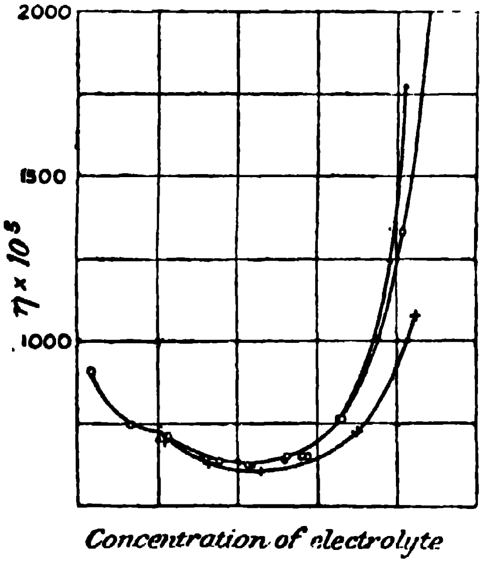


FIG. 52.

electrolyte it naturally dissolves in the continuous "water phase," and will exert osmotic pressure therein, the effect of which is to draw some water through the membrane of the disperse phase so that the concentration of water in the particles decreases, thereby causing the particles themselves to shrink in size, and hence exert a diminished effect upon the viscosity of the solution as a whole. This seems to be a reasonable explanation of the initial fall in viscosity. Another possible action of the electrolyte has to be taken into account, namely, the coagulating effect, such effect naturally becoming more pronounced the higher the concentration of the electrolyte. This causes the particles to coalesce, thereby forming larger aggregates, which produce an increase in the viscosity represented in Fig. 52, in the region of higher concentration of electrolyte. This view of the phenomena assumes that the larger the particles the greater the viscosity, and inversely. Woudstra (*loc. cit.*) has shown experimentally that this assumption is a correct one in the case of the inorganic colloids examined by him.

REVIEW OF THEORIES DEALING WITH THE STABILITY OF COLLOIDAL SOLUTIONS, AND THE MECHANISM OF COAGULATION.

In the first place we are concerned with the question of the stability of a colloidal solution, regarding it, in the most general terms, as a two-phase system, one phase being present in a finely divided state. We shall consider such a system from a purely physical standpoint. (The necessity of emphasising the term physical arises from the fact that a view of surface action has recently been propounded by Langmuir and by Harkins, which is essentially chemical in origin, capillary effects being attributed to residual valency. An account of the chemical theory is given in Chap. X. in connection with heterogeneous reaction velocity.)

From the general physical standpoint the problem of stability of a colloid system resolves itself into a problem of electro-capillarity, the equilibrium state depending upon capillary effects at the large interface, which separates the disperse phase from the medium, the capillary effects being modified by the presence of the electric charges on the particles of the disperse phase. A primitive attempt has been made by the writer to deal with the problem from this point of view (*Kolloid-Zeitschrift*, **5**, 91, 1909). No satisfactory theory, on this basis, has, as yet, been put forward.

Donnan, however (*Phil. Mag.*, **1**, 647, 1901) has attacked the problem from the standpoint of capillarity alone, the probable part played by the electrical charge not being considered. At the same time the importance of Donnan's conclusions warrants a short recapitulation here. The basis of Donnan's theory is the assumption that the range of molecular attraction (*i.e.* the distance throughout which the attraction due to a single molecule is still perceptible) varies from substance to substance. This is an extremely likely assumption. Suppose now we have a strip of substance A (*i.e.* the colloid substance) immersed in a liquid medium B (Fig. 53 (*a*) and (*b*)).

Consider a small particle or volume element X at the interface of A and B. Then the total attractive effect of B upon A may be represented by a large semicircle, its radius r being the range of the molecular attraction of the molecules composing B. Also the smaller semicircle, radius l, represents the attractive force pulling X into A. Suppose $r > l$. Now, if the strip of substance A be shaved down until it is very thin (until its thickness is as in Fig. 53 (*b*), in which the thickness is still greater than l, but less than r), then there will now be an effective portion of B pulling X in the opposite sense to its original effect, the extent of this oppositely directed effect being given by the shaded segment. The total effect of B upon X tending to draw it in the original direction is less than before, and we can evidently imagine that a critical value for the thickness of the strip may be reached at which the pull on X in opposite directions due to l and the "weakened" r effect would just balance one another. When this is reached there will be no further tendency of A to split into a finer state of division. For thickness greater than the critical, the body A has a tendency to *increase* its common surface with B, *i.e.* it possesses an effectively *negative* surface tension. For thickness less than the critical (l now greater than the *effective* r) there will be a positive surface tension, and hence smaller aggregates of A will tend to grow to the critical size. "If a colloid be defined as a substance which forms these pseudo-solutions termed colloidal, it follows from the above that this description is not sufficient unless the other medium—the pseudo-solvent—be specified. This point is well illustrated by the result obtained by Krafft with the soaps; these substances give true solutions with alcohol, and colloidal solutions with water." This possibility was first mentioned by W. B. Hardy.

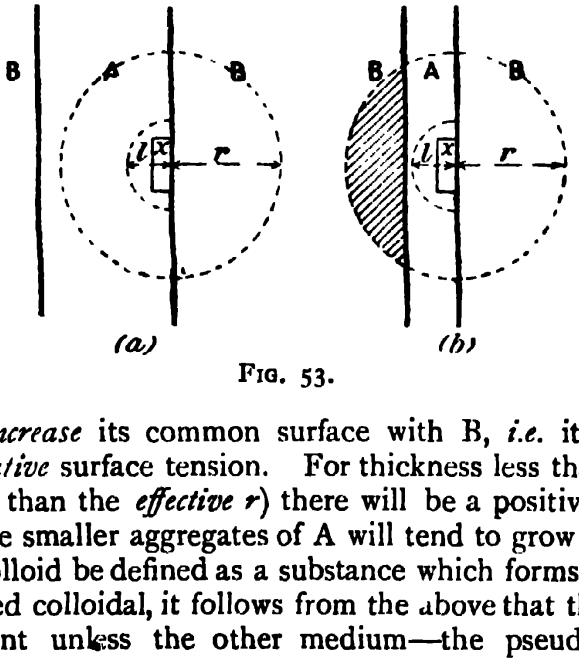


FIG. 53.

We now pass on to the attempts which have been made to account explicitly for the influences exerted by various substances present in the medium. In the first place, the experimental evidence now available shows pretty clearly that the electric charge which the particles in general carry—even in the case in which the medium was "originally" pure as in the case of colloidal platinum in pure water—is due to the preferential or selective adsorption of certain ions upon the surface of the particles. This act of selective adsorption of an ion appears to be essential for the permanent stability of the colloid.

In the second place we have to take account of substances artificially added to the medium. These are primarily ions, though they may also be the undissociated molecules of electrolytes, or molecules of non-electrolytes such as sucrose, or urea, or finally, other colloids. Such substances may either confer greater stability—an extreme case being the peptisation or formation of a sol from a substance which is already in the gel form—or, on the other hand, these substances may bring about coagulation.

In connection with the mechanism of coagulation, a number of different theories have been put forward from time to time, many of these theories, however, being little more than a restatement of some experimental fact, which itself requires an explanation.

First of all we have Hardy's theory. In this it is assumed that an electrical charge, *i.e.* a P.D. between the colloid and the medium, is necessary to the stability of the colloid. When by the addition of ions of opposite sign, such ions being selectively adsorbed, the colloid particle loses its P.D. with respect to the medium, the iso-electric point is reached and coagulation occurs. This would be an exceedingly useful generalisation if true, but it has now lost much of its significance in view of the work of Powis, already referred to, from which it appears that coagulation may take place before the iso-electric point is reached. This decidedly complicates matters. Hardy makes further assumptions about the electrical work required for the vibration of the colloid particles, which, however, are of a very hypothetical nature. Bredig has gone a step further in regarding the phenomenon as an electrocapillary one. Lippmann has shown that there is a connection between the surface tension at a phase surface and the charge on the surface. By altering the potential and plotting the corresponding values of surface tension, he obtained a curve which passed through a maximum value (for the surface tension) when the external E.M.F. was applied in a certain direction, *i.e.* when it was used to neutralise the natural P.D. possessed by the surface. When a surface is uncharged its surface tension is therefore greater than when it is charged. Hence at the iso-electric point, the surface tension on the colloid particle is a maximum. This may mean that the surface potential energy is a maximum, and according to Bredig coagulation occurs in order to reduce this, as will certainly happen since the surface area of the coagulated mass is much less than that of the free colloid particles. As regards the mechanism of the action of the precipitating electrolyte, Bredig applies Nernst's idea of the distribution of two ions between the phases, *viz.* the colloid particles and the medium. If these solubility coefficients are not the same for both ions then preferential solubility will occur, and hence set up a P.D. at the surface. If, therefore, the cation is more soluble in the colloid than the anion, it will tend to give a positive charge to the colloid, and if the latter is negative to start with the electrolyte may discharge it. Freundlich's theory is somewhat analogous to Bredig's with the important distinction, however, that instead of regarding the ions as *soluble* in the colloid, the effect is restricted to the surface. The P.D. is then set up by the preferential adsorption, or surface condensation of one ion to a greater extent than the other.

There is little doubt, then, but that selective adsorption is the main factor in the process of coagulation, being more important than the existence of electrical charge of opposite sign, as Bancroft has emphasised in criticising the Hardy-Schulze Law of coagulation.

At the same time we must not forget that, *in general*, ions of opposite sign to that possessed by a given colloid appear to be selectively adsorbed, and the more so the higher the valency. What is particularly significant for the selective adsorption view of coagulation is the fact that non-electrolytes can bring about coagulation. Urea, for example, is capable of effecting this in the case of certain colloids, and acetic acid is an excellent coagulant for rubber latex (an emulsion). In neither of these cases, presumably, are we dealing with ionic neutralisation of electric charge. Further, experiments on the settling of certain inorganic suspensions have shown that these may be precipitated by colloids having the same electrical sign as that of the suspension. It should be noted that the coagulants, in this case, *i.e.* starch, glue, albumen, are essentially substances which lower the interfacial tension.

In accepting the view that coagulation is due to selective adsorption, we have by no means cleared up all the difficulties. Let us consider substances which lower the surface tension of water, and the interfacial tension between the disperse phase and the medium. The lowering of tension leads of necessity to positive adsorption (compare Vol. II., Chap. XI.). Further, if the interfacial tension between the disperse phase and the medium be lowered by the added substance we would *not* expect coagulation to occur, for the total surface energy is now less than it was before. This is, in fact, the basis of Bredig's theory of the stability of colloid solutions. But the experiments on suspensions to which reference has been made show that coagulation is actually brought about by substances which lower the interfacial tension. We have here apparently a direct contradiction of our previous conclusion.

One point about which there is much uncertainty is whether the Brownian movement ceases just prior to coagulation. There is a rather general belief that such is the case. Svedberg (*Die Existenz der Molekule*, 1912, p. 105) has shown, however, that the intensity of the Brownian movement is not influenced by the addition of electrolytes. Of course, on the basis of the principle of equipartition of energy, which we have already employed in connection with Perrin's work on the Brownian movement (Chap. I.), it follows that the mean kinetic energy ($\frac{1}{2}MV^2$) of a single colloid particle at a given temperature must be the same as that of any coagulated *unit*, consisting of several particles, at the same temperature. In the latter case the mass term is greatly increased, and therefore the V^2 term, or the observable motion, is correspondingly diminished. We have in fact to distinguish clearly between the kinetic energy of the motion and the motion itself. In the state of affairs just prior to coagulation and just after adsorption of the ions has taken place upon the colloid particle—for it is fairly certain that several ions would be required to neutralise the charge on the colloid particle (*cf.* Lewis, *Kolloid-Zeitschrift*, **4**, 209, 1909)—in this state, the mere addition of a number of ions to a relatively massive colloid particle could not affect its mass sensibly, and therefore must leave the motion as vigorous as before. If, however, the ions are heavily hydrated—and we would expect this in the case of polyvalent ions such as $Al^{\cdots}$—the increase in mass, due to the adsorption of a number of these ions along with their atmosphere of adhering water molecules, might be sufficiently great to lower the V^2 term sensibly and therefore give rise to the visual effect of diminished motion. This, however, is somewhat hypothetical, but it is a matter for exact experimental investigation. In general the question arises—to what extent is the Brownian movement responsible for the stability of the colloid, and what part does it play in the act of coagulation? We shall return to this later.

The idea of selective adsorption has been brought into account for stability, coagulation, reversal of coagulation, and the closely allied phenomenon of peptisation. Whilst all this is certainly correct, it is obvious that much remains to be done to give precision to the idea. At present selective adsorption is a useful qualitative hypothesis; future research must concern itself with the formulation of selective adsorption as an exact quantitative theory.

Although a certain amount of agreement has been reached in regard to the question of stability and of coagulation, our knowledge is far from being complete. The present position with regard to stability may be expressed as follows (*cf.* Bancroft, *Journ. Amer. Electrochem. Soc.*, **27**, 175, 1915):—

"Any substance may be brought into a state of colloidal solution provided we make the particles of that phase so small that the Brownian movements will keep the particles suspended, and provided we prevent coagulation of the particles by a suitable surface film (*cf. Journ. Phys. Chem.*, **18**, 552, 1914). Coalescence may be prevented by a non-electrical film, by an electrical film, electrical charge, or by any combination of the two."

For further information upon colloid chemistry in general, the reader should consult Müller's *Allgemeine Chemie der Kolloide* (Bredig's Series of Textbooks of Applied Physical Chemistry), H. Freundlich's *Kapillarchemie*, Zsigmondy's *The Ultramicroscope*, Wolfgang Ostwald's *Grundriss der Kolloidchemie*, Burton's *Physical Properties of Colloidal Solutions*, W. W. Taylor's *Chemistry of Colloids*, and the various volumes of the *Zeitschrift für Chemie und Industrie der Kolloide* ("*Kolloid-Zeitschrift*").

For technical applications of colloid chemistry the reader is referred to a short summary by W. C. M. Lewis (*Journ. Soc. Chem. Ind.*, No. 10, Vol. XXXV., 1916) and particularly to a series of Reports on Colloid Chemistry and its applications edited by a Committee of the British Association and published by H.M. Stationery Office.

CHAPTER IX.

Systems not in equilibrium—Treatment from the kinetic standpoint—*Homogeneous Systems:* Diffusion of solutes in a solution—Reaction velocity — Types of reactions—Catalysis.

Diffusion of Solutes in Solution.[1]—The motion of a dissolved substance from one part of a solution to another represents the simplest type of "chemical" kinetics in a homogeneous system. It was first quantitatively examined by Nernst (*Zeitsch. physik. Chem.*, **2**, 613, 1888), who employed as a fundamental assumption the validity of Fick's Law (*Pogg. Ann.*, **94**, 59, 1855), *viz.* the quantity of salt which diffuses through a given area is proportional to the difference between the concentrations at two areas infinitely near to each other. That is, if we take two points in a solution at an infinitesimal distance apart dx, the difference in concentration at these two points will be dc, and hence the concentration gradient in the direction x will be $\frac{\partial c}{\partial x}$. *Fick's Law* states that, for the case when the diffusion is in one direction only, as occurs when it is allowed to take place in a cylinder, the amount of solute $d\mathrm{S}$ which will cross a given cross-section area a, in a time dt, is expressed by—

$$d\mathrm{S} = -\mathrm{D}a\frac{\partial c}{\partial x}dt \quad . \quad . \quad . \quad . \quad (1)$$

or the rate of change by—

$$\frac{d\mathrm{S}}{dt} = -\mathrm{D}a\frac{\partial c}{\partial x} \quad . \quad . \quad . \quad . \quad (2)$$

The minus sign here denotes that the solute diffuses in the direction of decreasing concentration. *D is the so-called diffusion constant or specific diffusion rate; it is equal to the amount of solute which would diffuse across unit area under a concentration gradient of unity in unit time if the rate were constant during that time.* In this section the time is expressed in days, the concentration in equivalents per liter, and the distance in centimetres. Now consider an infinitesimal volume in a cylinder bounded by planes at the distance x and $x + dx$. The amount of solute which will accumulate in this volume in time dt will be the difference in the amount which will cross the planes at x and at $x + dx$. That is—

---

[1] See R. Haskell (*Physical Review*, **27**, 145, 1908), from whose paper this section is mainly taken.

$$\left[dS - \left(dS + \frac{\partial(dS)}{\partial x}dx\right)\right] \text{ or } - \frac{\partial(dS)}{\partial x}dx.$$

The increase in concentration of the solute in time dt in this volume, then, is the total accumulation divided by the volume, or—

$$\frac{-\dfrac{\partial(dS)}{\partial x}dx.}{adx}$$

As this may also be expressed by the quantity $\frac{\partial c}{\partial t} . dt$, we get—

$$\frac{\partial c}{\partial t}dt = -\frac{1}{a}\frac{\partial(dS)}{\partial x}.$$

Substituting for dS its value $- \mathrm{D} . a . \frac{\partial c}{\partial x} . dt$ given by Fick's Law, carrying out the differentiation, and eliminating dt, we obtain as our reduced equation for the case, in which the cross-section is uniform—

$$\frac{\partial c}{\partial t} = \mathrm{D}\frac{\partial^2 c}{\partial x^2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation is analogous to that of Fourier for the flow of heat, and has different solutions according to the conditions imposed by the methods of carrying out the diffusion. If in a tube so long as to be practically infinite, so far as the time of an ordinary experiment is concerned, the concentration is held constant at one end and is zero at the other, and if at the start the concentration is zero throughout the tube, we may obtain by solving the differential equation under the assumption that D is constant the following expression for the concentration c at any point x after any time t—

$$c = c_0\left(1 - \frac{2}{\sqrt{\pi}}\int_0^u e^{-u^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where c_0 is the concentration at the lower end, and—

$$u = \frac{x}{2\sqrt{\mathrm{D}t}}.$$

Knowing the value c for any point we can inversely calculate D, the diffusion constant. If D is not constant for all values of c, as is the case if the assumption of the different rates of diffusion of the dissociated and undissociated substances is true, another formula must be developed which will take this fact into consideration.

Nernst considers the case of electrolytes which he assumes to be completely dissociated. In this way we have to deal with only one diffusion coefficient, since the electrical force practically prevents the ions separating, and the slow one is hastened, the faster one delayed, so that both travel together. Assuming the solute to be totally dissociated, Nernst derived theoretically an expression for D in terms of the ionic velocities as computed from transference and conductivity data for the case of a salt splitting into two univalent ions. For the more general case in which the salt is completely dissociated into any number of ions, an expression may be similarly derived,[1] as follows:—

Let us take an electrolyte whose molar weight yields on complete dissociation n_c mols of cations of valence v_c and n_a mols of anions of valence v_a. The product of the number of mols of each ion by its valence is necessarily the same for both the positive and negative ions (for electric neutrality); or $n_c v_c = n_a v_a$. If C is the concentration of salt in mols per liter, the number of ions having the same electrical sign is n_cC for the cation and n_aC for the anion (*i.e.* n_cC or n_aC = gram-ions or mols per liter); and correspondingly the concentration gradients for the cation and anion are $\frac{n_c dC}{dx}$ and $\frac{n_a dC}{dx}$, respectively. As the osmotic pressure of the ions is expressed by $P = n\mathrm{CRT}$, the force acting across unit area through the distance dx in the positive direction of x is the difference between the force P at x and $P + dP$ at $x + dx$, or is—

$$- n_a \mathrm{RT}\frac{d\mathrm{C}}{dx}dx \text{ and } - n_c \mathrm{RT}\frac{d\mathrm{C}}{dx}dx$$

for the anions and cations respectively. This is the force that acts upon the ions in the volume dx (the sectional area being unity), that is upon $n_a\mathrm{C}dx$ and $n_c\mathrm{C}dx$ mols of anions and cations, so that the force acting upon one mol will be—

$$\frac{- n_a \mathrm{RT}\frac{d\mathrm{C}}{dx}dx}{n_a \mathrm{C}dx} = \frac{- n_c \mathrm{RT}\frac{d\mathrm{C}}{dx}dx}{n_c \mathrm{C}dx} = - \frac{\mathrm{RT}}{\mathrm{C}} \cdot \frac{d\mathrm{C}}{dx} \quad . \quad . \quad (5)$$

it being therefore identical for both the anion and cation. Now, since the friction against the solvent is different for the different ions, one ion would tend to get ahead of the other. This, however, would generate an electrostatic field between the positive and negative ions, which field in turn would accelerate the slower ion and retard the more rapidly moving one. Let us consider the electric potential generated to be E, then the electric force acting upon one mol of cation or anion is—

$$- v_c \mathrm{F}\frac{d\mathrm{E}}{dx} \text{ or } + v_a \mathrm{F}\frac{d\mathrm{E}}{dx}$$

respectively, where F is one faraday of electricity. The total force acting upon one gram ion or mol therefore is—

---

[1] For this derivation Haskell is indebted to Professor A. A. Noyes. Since it is cast in an extremely neat form I quote it practically word for word.

$$-\mathrm{RT}\frac{1}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}-v_c\mathrm{F}\frac{d\mathrm{E}}{dx}\text{ for the cations}\quad . \quad . \quad (6)$$

$$-\mathrm{RT}\frac{1}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}+v_a\mathrm{F}\frac{d\mathrm{E}}{dx}\text{ for the anions}\quad . \quad . \quad (7)$$

Let u_c and u_a be the velocities of each ion when the force acting upon one mol or gram ion is unity, and let $d\mathrm{N}_c$ and $d\mathrm{N}_a$ be the number of gram ions of each ion passing a cross-section a in time dt, then under the above force—

$$d\mathrm{N}_c = u_c a n_c \mathrm{C}\left(-\mathrm{RT}\frac{1}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}-v_c\mathrm{F}\frac{d\mathrm{E}}{dx}\right)dt^{1}\quad . \quad . \quad (8)$$

$$d\mathrm{N}_a = u_a a n_a \mathrm{C}\left(-\mathrm{RT}\frac{1}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}+v_a\mathrm{F}\frac{d\mathrm{E}}{dx}\right)dt\quad . \quad . \quad (9)$$

But $\dfrac{d\mathrm{N}_c}{n_c}$ = the fraction of one gram ion of the cations passing the section in time dt. $\dfrac{d\mathrm{N}_a}{n_a}$ has the same significance for the anion. Therefore—

$$\frac{d\mathrm{N}_c}{n_c}=\frac{d\mathrm{N}_a}{n_a}.\quad . \quad . \quad . \quad . \quad . \quad (10)$$

since equivalent quantities of the two ions must pass through any section in the same time, it follows that—

$$u_c\left(\mathrm{RT}\frac{1}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}+v_c\mathrm{F}\frac{d\mathrm{E}}{dx}\right)=u_a\left(\mathrm{RT}\frac{1}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}-v_a\mathrm{F}\frac{d\mathrm{E}}{dx}\right)\quad . \quad (11)$$

or

$$\mathrm{F}\frac{d\mathrm{E}}{dx}=-\left(\frac{u_c-u_a}{u_c v_c+u_a v_a}\right)\frac{\mathrm{RT}}{\mathrm{C}}\cdot\frac{d\mathrm{C}}{dx}\quad . \quad (12)$$

If this value be substituted in equation (8) or (9), and further substitution be made in equation (10) above, we have—

$$\frac{d\mathrm{N}_a}{n_a}=\frac{d\mathrm{N}_c}{n_c}=\left\{\begin{matrix}d\mathrm{N}\\ \text{or}\\ d\mathrm{S}\end{matrix}\right\}=-a\mathrm{RT}\frac{d\mathrm{C}}{dx}\left\{\frac{u_a u_c(v_a+v_c)}{u_c v_c+u_a v_a}\right\}dt\quad . \quad (13)$$

where $d\mathrm{N}$ or $d\mathrm{S}$ is the number of molar weights passing cross-section in time dt. By comparison of (13) with (1) we see that—

$$\mathrm{D}=\mathrm{RT}\left\{\frac{u_a u_c(v_a+v_c)}{u_c v_c+u_a v_a}\right\}.$$

---

[1] For u_c = velocity of ion = number of cms. traversed by the ion per second. $u_c a$ = *volume* of solution swept out, *i.e.* passing over a plane in unit time. If concentration is $n_c\mathrm{C}$, *i.e.* the number in unit volume, then $n_c\mathrm{C} \times u_c a$ = number of gram ions passing through the plane per unit time when under unit force. With above force the number $d\mathrm{N}c$ in time dt is $n_c\mathrm{C}u_c a$ × total force × dt.

If instead of molar weights we use equivalent weights, since one molar weight equals $n_c v_c$ or $n_a v_a$ equivalents, and $U_c = u_c v_c$ and $U_a = u_a v_a$ represent the velocities when unit force acts on one equivalent weight of ions,[1] we obtain by substitution and reduction—

$$dS = -aRT\frac{dc}{dx}\cdot\frac{U_aU_c}{U_a + U_c}\left(\frac{1}{v_c} + \frac{1}{v_a}\right)dt \quad . \quad . \quad (14)$$

where dS is the number of equivalents crossing in time dt, and where $\frac{dc}{dx}$ represents the concentration gradient in equivalents.

By a comparison of this formula with the expression of Fick's Law (equation (1)), we see that we can express D in terms of quantities derived from electrical measurements, or—

$$D = RT\frac{U_aU_c}{U_a + U_c}\left(\frac{1}{v_c} + \frac{1}{v_a}\right) \quad . \quad . \quad . \quad (15)$$

provided, of course, we assume that the solute is totally dissociated, and hence all diffusion is done by the ions only. This condition is approached only in very dilute solutions, and hence D is the limiting value at infinite dilution. At other concentrations the value of D as found from Fick's formula will be greater or less according as the undissociated substance diffuses faster or slower than the ions. *As a general rule, the diffusion constant has been shown to become larger as the dilution is increased, and hence, we believe that the ions move more rapidly than the undissociated portion.*

The typical experimental arrangement for investigating the above expression consists of a long vertical cylinder, with solid salt at the bottom, the diffusion takes place upwards. The retarding influence of gravity Haskell shows to be negligible, and the above arrangement has the advantage of keeping the denser portions of the solution at the bottom, so that no stirring or mixing effects enter. The tube is of such a length that the experiment can be completed—the time is measured in days—before any salt reaches the top. The concentration at different levels can be determined, by measuring the electrical conductivity, by means of small electrodes situated in pairs at various heights in the tube. This was the general arrangement employed, for example, by Haskell.

---

[1] If unit force acts on one equivalent, then v_c times this force acts on one *mol* or gram ion. If u_c be velocity of the cation when unit force acts on one equivalent of the ion, then $v_c u_c$ is the velocity when the above force acts on one gram ion, for velocity ∝ force always.

Öholm's Diffusion Constant Data at 18° C. (*Zeitsch. phys. Chem.*, **50**, 309, 1905). [These values were obtained graphically from actual determinations carried out at different temperatures in the neighbourhood of 18° C.]

Normality.	NaCl.	KCl.	LiCl.	KI.	HCl.	$CH_3.COOH$.	NaOH.	KOH.
5·5	1·065	—	—	1·549	—	—	—	—
4·2	—	—	0·956	—	—	—	—	—
3·6	—	1·338	—	—	—	—	—	—
2·8	1·064	—	—	1·434	—	—	—	—
2·00	—	1·320	0·928	—	—	—	1·259	1·892
1·00	1·070	1·330	0·920	1·366	2·217	0·833	1·290	1·855
0·50	1·077	1·345	0·919	1·372	2·188	0·856	1·310	1·841
0·20	1·098	1·367	0·929	1·380	2·202	0·871	1·342	1·843
0·10	1·117	1·389	0·951	1·391	2·229	0·884	1·364	1·854
0·05	1·139	1·409	0·971	1·412	2·251	0·895	1·386	1·872
0·02	1·152	1·431	0·980	1·428	2·285	0·910	1·404	1·889
0·01	1·170	1·460	1·000	1·460	2·324	0·930	1·432	1·903

The values of D at concentration 0·01 N may be taken as referring to practically complete dissociation of the substance in all cases except that of the weak acid $CH_3.COOH$. The following are some of the values of D calculated and observed:—

Substance.	D_{18} Observed (Öholm).	D_{18} Calculated (Öholm).
NaCl	1·170	1·173
KCl	1·460	1·460
LiCl	1·000	0·994
KI	1·460	1·467
HCl	2·324	2·431
$CH_3.COOH$ . .	0·930	1·368
NaOH	1·432	1·558
KOH	1·903	2·109

The agreement is good, and the relation between mobility of ions under an electric field, and diffusion under no external field as given by the expression for D is therefore justified.

Öholm's Determination of the Temperature Coefficient of Diffusion.—If D_{t_0} and D_{t_1} be the diffusion coefficients for a given substance at temperatures t_0 and t_1 respectively, then the temperature coefficient α is given by the expression—

$$\alpha(t_1 - t_0) = \frac{D_{t_1} - D_{t_0}}{D}$$

or

$$\frac{D_{t_1}}{D_{t_0}} = 1 + \alpha(t_1 - t_0).$$

In this expression α is the fractional increase in D due to 1° rise in temperature. α is usually given as the fractional increase in D for 10°

rise in temperature, and the following values for a have this significance. The reason for adopting this convention here is to bring the results into line with the temperature coefficients of purely chemical reactions (p. 409 *seq.*) and of heterogeneous catalytic reactions (p. 450 *seq.*). The following values are calculated from Öholm's mean values (*l.c.*, p. 331):—

Substance.	a.	$\frac{D_{t_0+10}}{D_{t_0}}$.
NaCl	0·25	1·25
KCl	0·235	1·235
LiCl	0·27	1·27
KI	0·235	1·235
HCl	0·19	1·19
$CH_3.COOH$ . .	0·28	1·28
NaOH . . .	0·23	1·23
KOH	0·21	1·21

Öholm points out that the smaller the diffusion constant D is, the greater is the value of the temperature coefficient of D. The same relation holds good for the electrolytic conductivity of these substances and its temperature coefficient. In fact, Öholm concluded that the temperature coefficient of diffusion was equal to the sum of the temperature coefficient of the osmotic pressure (identical in dilute solutions with the temperature coefficient of gaseous expansion) + the temperature coefficient of the electrical conductivity.

Haskell has studied more closely the case of a dissociated solute diffusing in two parts, the dissociated and the undissociated. During an infinitesimal time the parts may be considered as moving independently, each having its own diffusion coefficient.[1] Hence we can say that the total amount crossing the area is equal to the sum of the two parts, that is—

$$dS = dS_1 + dS_2.$$

Haskell works out a differential expression for this which, however, he cannot integrate. He therefore has to employ approximate methods of solution by introducing empirical relationships connecting x, t, and c in his experiments with thallium sulphate and barium nitrate. These salts were investigated in decinormal solutions, and are to a large extent undissociated. The results obtained were as follows:—

Salt.	D_1 Unionised Salt.	D_2 Ions.
Tl_2SO_4	0·77 0·80 } Mean 0·785	1·56 1·50 } Mean 1·53
$Ba(NO_3)_2$	0·69	1·40

---

[1] Nernst, *Zeitsch. phys. Chem.*, 2, 634, 1888.

It is thus seen that the rate of diffusion of the undissociated substance is one-half that of the ions. The friction encountered by the molecules is therefore double that encountered by the ions.

REACTION VELOCITY IN HOMOGENEOUS SYSTEMS.

We may have two cases:—

(1) Isolated reactions, *i.e.* a single reaction unaccompanied by any side reaction, and

(2) Simultaneous reactions.

1. *Isolated Reactions.*

By way of introduction it may be necessary to define fairly rigidly what is meant by the velocity of a chemical reaction. The first thing to be noted about practically all chemical reactions is that they do not progress at a constant rate. They start off rapidly under certain given conditions, and as time goes on the reaction becomes slower. A determination of the quantity of substance transformed divided by the time taken would therefore not give us a reliable numerical value characteristic of the reaction, for the value would evidently vary with the *stage* at which we examined the reaction. What we must attempt to do, therefore, is to connect the infinite number of different instantaneous velocities—each of which we denote by the symbol $\frac{dx}{dt}$, where x is the amount of substance transformed—together by some expression or law, in the form of a differential equation, which after integration will give us some numerical value or values—a constant or constants, in fact—characteristic of the processes under investigation. The law referred to is the Law of Mass Action, and in its most general form, as applied to chemical kinetics, may be defined as follows:—

The rate at which a body takes part in a chemical reaction is proportional to its active mass. When we are dealing with a system in which the term "concentration of a component" has a definite meaning, and this type of system is the usual one in homogeneous chemical kinetics—in such a case the most general form of the Law of Mass Action may be expressed thus: The rate at which a substance takes part in a reaction is proportional to its concentration raised to a certain power—this power being numerically identical with the number of molecules of the substance required to satisfy the chemical equation which represents the reaction. Thus let us take the case of water decomposing into hydrogen and oxygen. The stoicheiometric equation is—

$$2H_2O \rightarrow 2H_2 + O_2$$

and the law of mass action states, therefore, that the rate at which the water molecules participate is proportional to $C^2_{H_2O}$, the rate at which H_2 molecules participate (in tending to reform water) is proportional to $C^2_{H_2}$, and the rate at which the oxygen molecules tend to participate is simply proportional to C_{O_2}. The simplest conceivable measure of the reactivity of a substance is, of course, to put it proportional to the concentration. A reaction such as that above can then be rewritten—

$$H_2O + H_2O \rightarrow H_2 + H_2 + O_2$$

and we might regard each constituent represented by each molecular symbol as different—though the process is rather artificial—when we see at once that the rate at which the constituents of the left-hand side are reacting is $\propto C_{H_2O} \times C_{H_2O}$, which gives us again the form $C^2_{H_2O}$. Similarly in the case of the H_2 molecules we arrive at the expression $C^2_{H_2}$ as the measure of the reactivity of H_2 in this reaction.[1]

Chemical reactions are conveniently divided into classes according to their stoicheiometric equations, and consist of one molecule, two, three, etc., giving rise to any number of resultants. The names employed are monomolecular, bimolecular, termolecular, etc. We shall consider these in order.

Monomolecular Reactions.—We would expect, on general grounds, to find the simplest cases of monomolecular reactions in the gaseous state. It is a significant fact, however, that not a single case of such a reaction (of the ordinary chemical kind), which proceeds at a measurable rate, is met with in gaseous systems. Certain monomolecular radio-active changes will be mentioned later. Bimolecular reactions, on the other hand, occur frequently. It appears that spontaneous decomposition of a single gas molecule does not occur easily, being realised only at relatively high temperatures, at which the rate of decomposition is too great to be measured. Turning then to liquid systems we find a number of apparently monomolecular reactions, but on closer inspection none of these represents in a simple and satisfactory manner the particular type of reaction which we have in view for the moment, *viz.* a true monomolecular reaction which proceeds to completion without any secondary effect entering into the process.

The decomposition of dibromo-succinic acid into a bromo-maleic acid and hydrobromic acid according to the equation—

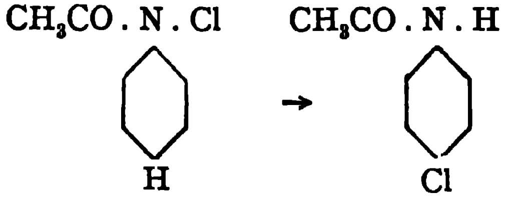
$$C_4H_4O_4Br_2 = C_4H_3O_4Br + HBr,$$

is a monomolecular reaction as far as this stoicheiometric equation is concerned, and as a matter of fact, over a certain range a satisfactory monomolecular "velocity constant" is obtained. If, however, we allow the reaction to proceed for a sufficiently long time we find that the values obtained for the velocity constant at successive time intervals gradually decrease. This is due to the fact that the reaction is reversible to a certain extent, *i.e.* the hydrobromic and bromo-maleic acids react together to give dibromo-succinic acid, and this naturally introduces a complication which is not allowed for in the very simple considerations with which we are immediately concerned.

---

[1] Or, on the theory of probability, the chance that two molecules A and B come into contact is proportional to the product of their concentrations.

Another reaction which is sometimes cited as an example of a simple monomolecular type is the transformation of dissolved acetochloranilide into p-chloro-acetanilide, according to the scheme—



Experiment has shown that over a certain range of concentration and temperature a good monomolecular velocity constant is obtained, but on changing the conditions the constant exhibits a marked rise or fall (unpublished experiments of A. Holt). This behaviour is in itself evidence that the reaction does not proceed in the very simple manner suggested by the above scheme, and incidentally this illustrates the usefulness of the measurement of velocity constants as a method of investigating the mechanism of a given reaction. The above reaction has been studied in detail by Orton (*Brit. Assoc. Reports*, 1910 and 1913),[1] and without going into details it may be said that the above process really involves three distinct reactions. In general it appears that these reactions which involve the shift of an atom or group from one part of a molecule to another are in reality complex, consisting of two or more successive processes.

The most satisfactory illustrations of a monomolecular velocity constant are to be found in the hydrolysis of carbohydrates, such as sucrose, which will be referred to later. In these cases, however, we are not dealing with the decomposition of a single molecule, but in reality with the interaction of two kinds of molecules. That is, such reactions are bimolecular as far as the *stoicheiometric* equation is concerned, but proceed as though they were monomolecular (under certain conditions) as far as the *velocity* equation is concerned. We have here an instance of a fact often met with, namely, that the stoicheiometric equation does not necessarily coincide with the actual velocity equation. It is, of course, the latter which expresses the real mechanism of the process. In the case of bimolecular reactions we find frequently that the stoicheiometric and the velocity equations are identical.

As a sufficiently unequivocal illustration is not available in actual practice, let us take the hypothetical case of a substance A which decomposes spontaneously into any number of resultants at a measurable rate, and further let us suppose that the reaction goes to completion, *i.e.* until there is no longer any of the reactant A left in the system.

According to the law of mass action the rate at which the substance A is participating, *i.e.* disappearing, at any moment is proportional to its concentration (for the power to which the concentration term is to be raised is unity). This may be written in the form of a differential equation

---

[1] Under the heading "Report of a Committee on the Transformation of Aromatic Nitroamines and Allied Substances".

$$\frac{dx}{dt} = k(a - x)$$

—where x is the amount of the substance A transformed at any time, a is the original quantity started with, $(a - x)$ being the amount left at any time t, and k is a constant. We want to evaluate k, and to do so it is evidently necessary to integrate the equation. This is done as follows:—

The expression $$\frac{dx}{dt} = \frac{-d(a - x)}{dt}$$

and therefore $$\frac{-d(a - x)}{dt} = k(a - x) \text{ or } \frac{-d(a - x)}{a - x} = kdt$$

or $$-\log (a - x) = kt + \text{constant of integration.}$$

When $t = 0$ (the starting time) $x = 0$ (no reaction has occurred), and hence applying the above integration expression to this point, it is evident that the constant of integration $= -\log a$. Hence the integrated expression may be written—

$$-\log (a - x) + \log a = kt$$

$$\text{or} \quad \frac{1}{t} \log \frac{a}{a - x} = k.$$

This expression can be used to evaluate k.

A similar type of reaction velocity, perhaps more correctly a heterogeneous reaction velocity, is exemplified by many radio-active transformations, notably the decay of thorium X with time (when isolated from thoria itself) investigated by Rutherford and Soddy (*Trans. Chem. Soc.*, **81**, 837, 1898). If we omit the initial part of the process for reasons which will be clear when we have studied so-called "consecutive simultaneous reactions" (page 402), the following data are given for the rate of decay of isolated Th X (deposited on a platinum wire, say). The units are of course arbitrary.

Time in Days from Start.	Activity of Th X.
2	100
3	88
4	72
6	53
9	29·5
10	25·2
13	15·2
15	11·1

In this case a is $= 100$. Employing the expression $k = \frac{1}{t} \log \frac{a}{a -}$ we obtain the following results :—

t Intervals.	$a - x$.	$\frac{1}{t} 2{\cdot}3 \log_{10} \frac{a}{a-x} = k$.
0 = {arbitrary initial point}	100	—
1	88	(0·128)
2	72	0·168
4	53	0·159
7	29·5	0·174
8	25·2	0·172
11	15·2	0·171
13	11·1	0·169
		Mean = 0·169

Another instance is afforded, in the case of the rate of decay of radium emanation (niton).

Decay of Radium Emanation (Rutherford and Soddy, *Phil. Mag.*, [6], **5**, 445, 1903).—The emanation—which is itself a gas—mixed with air was obtained from a solution of radium chloride and kept in a closed bottle. It was stored over mercury in an ordinary gasholder. From time to time equal quantities were measured off by a gas pipette and delivered into the testing vessel, which consisted of a brass cylinder having a central isulated electrode. A sufficient voltage to obtain the saturation current was applied between the central rod and the cylindrical shell, the central rod being at the same time connected to an electrometer. The ionisation current immediately after the introduction of the emanation furnished a measure of the activity of the latter. The measurements were repeated over a period of 33 days before the effect became too small to be accurately determined. The following results were obtained :—

Time in Hours.	Relative Activity of the Emanation.
0	100
20·8	85·7
187·6	24·0
354·9	6·9
521·9	1·5
786·9	0·19

From the above values it may be observed that the activity falls off in a geometrical progression with the time; the time taken for the activity to fall to half its original value being 3·71 days, this result being obtained by substituting in the simple exponential or monomolecular expression—

$$I = I_0 e^{-\lambda t} \text{ or } \frac{1}{t} \log \frac{I_0}{I} = \lambda$$

where I_0 is the initial activity (measured by the magnitude of the saturation current), and I the activity after time *t*.

A recent determination of the rate of decay of radium emanation is that given by Rümelin (*Phil. Mag.*, **14**, 550, 1907), who found that the period of half decay was 3·75 days; Ramsay has, however, found 3·18.

Rate of Formation of Radium Emanation (Rutherford and Soddy, *loc. cit.*).—Radium chloride was dissolved in water and a current of air aspirated through the solution. After a few hours the radio-activity of the salt obtained from the solution was found to have been reduced to a minimum, and continued aspiration over three weeks did not affect it. It was inferred, therefore, that all the emanation had been removed, and now it was possible, after evaporating the solution to dryness, to determine the rate of formation of the emanation by measuring the activity of the radium salt at different intervals of time. The following results were obtained:—

Time in Days.	Activity.	Per Cent. Activity Recovered.
0	25·0 {the non-separable activity}	0
0·70	33·7	11·7
1·77	42·7	23·7
4·75	68·5	58·0
7·83	83·5	78·0
16·0	96·0	95·0
21·0	100·0	100·0

The two sets of values corresponding to the decay of the emanation and its rate of formation were found to be exactly complementary.

Another important monomolecular reaction which takes place in aqueous solution, especially in the presence of acid, is the inversion of cane sugar into dextrose and lævulose according to the equation—

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{lævulose}}{C_6H_{12}O_6}$$

The reaction is catalysed, *i.e.* hastened, by the presence of $H^{\cdot}$, and its velocity may indeed be used as a measure of the concentration of the latter. It might appear at first sight that this is a bimolecular reaction as is certainly the case according to the stoicheiometric equation, for in all, two molecules appear on the left-hand side. The rate of the reaction may therefore be written $\propto C_{\text{sugar}} \times C_{H_2O}$. But since the C_{H_2O} is constant at all stages of the reaction (since we are dealing with dilute aqueous solution), the term C_{H_2O} may be moved into the factor of proportionality, and we conclude that the rate at which the reaction proceeds is simply proportional to the concentration of cane sugar—and as only one molecule of this is involved in the stoicheiometric equation, the power to which the concentration term is raised is unity. Hence for the inversion of cane sugar—which can be followed experimentally in a polarimeter, since the products of the reaction, *i.e.* the resultants dextrose and lævulose, rotate the beam of polarised light in a different direction to cane sugar—we find the expression

$$\frac{1}{t} \log \frac{a}{a - x} = k$$

gives actually constant values for k, and hence the reaction is monomolecular. The following results may be given by way of illustration:—

INVERSION OF CANE SUGAR. $a = 10{\cdot}023$.

t Mins.	x.	k.
0	0	-·-
30	1·001	0·00152
60	1·946	0·00156
90	2·770	0·00156
130	3·726	0·00155
180	4·676	0·00151

One must be on one's guard, therefore, in studying a new reaction, in attempting to find out from the nature of the velocity constant, how many molecules are taking part. Often the velocity constant does actually tell us how many molecules take part, but it is also seen from the above illustration that a substance may be actually taking part in the mechanism of the reaction, but if its concentration is not thereby affected, *e.g.* the water, its presence will not be made clear, in the type of velocity constant obtained.

The above remarks must not be regarded as standing in contradiction to an earlier statement, *viz.* that the velocity equation expresses the real mechanism of the process. In the above case we have the special condition that the water-concentration is a fixed or constant quantity. What the velocity equation expresses in such a case is that the reaction is monomolecular with respect to the sucrose, *i.e.* one molecule and one molecule only of the sucrose reacts with a water molecule to give lævulose and dextrose. If we were to allow the above process to occur, say, in an acetone solution containing *limited* quantities of both water and sucrose, a monomolecular velocity constant would no longer be obtained; the reaction would now function as a true bimolecular one, since the concentration of both water and sucrose alters appreciably during the course of the reaction.

Now let us consider bimolecular reactions.

Bimolecular Reactions.—These may be represented by—

$$2A \rightarrow \text{one or more resultants}$$

or

$$A + B \rightarrow \text{,, ,, ,, ,,}$$

A typical instance is the saponification of an ester by an alkali, *e.g.* ethyl acetate and caustic soda[1] in aqueous solution reacting nominally according to the equation—

$$CH_3.COOC_2H_5 + NaOH \rightarrow CH_3.COONa + C_2H_5.OH.$$

During the reaction the concentration of both the alkali and ester decreases, and since the equation involves only one molecule of each, we see by the law of mass action that the rate at which the resultants are being formed is—

$$\frac{dx}{dt} = kC_{CH_3 \cdot COOC_2H_5} \times C_{NaOH}.$$

The reaction is a bimolecular one.

Suppose we start with equivalent amounts of ester and alkali, say a gram-moles in a certain volume which remains constant throughout the reaction, and let x be the amount of each transformed at time t, then the velocity expression is—

$$\frac{dx}{dt} = k(a - x)(a - x) = k(a - x)^2.$$

---

[1] That it is the hydroxyl ion and not the undissociated molecule of the alkali which effects the hydrolysis is shown fairly clearly by the fact that solutions of *different* alkalis (KOH, NaOH, $Ba(OH)_2$, etc.), at the same equivalent concentration, *i.e.* the same hydroxyl ion concentration, cause the reaction to proceed at approximately the same rate. Further, if it were the undissociated molecule of the alkali which was involved, then in the case of baryta the reaction would be—

$$2CH_3COOC_2H_5 + Ba(OH)_2 = (CH_3COO)_2Ba + 2C_2H_5OH.$$

This reaction would be ter-molecular, as it involves two molecules of ester and one of alkali. A ter-molecular velocity constant is not obtained, however, the reaction being bimolecular. This is most easily explained by writing the actual process in all cases as—

$$CH_3COOC_2H_5 + OH' = CH_3COO' + C_2H_5OH$$

or in a more complete form (in the case of caustic soda)—

$$CH_3COOC_2H_5 + Na^{\cdot} + OH' = CH_3COO' + Na^{\cdot} + C_2H_5OH.$$

In sufficiently dilute solution the caustic soda and the sodium acetate, being strong electrolytes, are very largely dissociated. If the dissociation is very large the concentration of OH ions will vary in nearly the same proportion as the total alkali present, reckoned as NaOH. (This would not be the case, of course, for a weak base such as ammonia.) This is the justification for expressing the above reaction in the form—

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

The NaOH term here represents titratable base, and at all stages this term is proportional to the OH′ concentration approximately. It is to be noted further that in the saponification of an ester by alkali the reaction proceeds to completion, no unchanged ester remaining at the end. When the ester is saponified or hydrolysed by water in the presence of H ions the end point is really an equilibrium point at which all four substances, ester, water, acid, alcohol, are present.

To obtain k we must integrate this expression. As before—

$$\frac{dx}{dt} = \frac{-d(a-x)}{dt}$$

and hence $\frac{-d(a-x)}{dt} = k(a-x)^2$ or $\frac{-d(a-x)}{(a-x)^2} = kdt$

and therefore $\frac{1}{a-x} = kt +$ integration constant.

When $t = 0$ $x = 0$, and therefore the integration constant $= \frac{1}{a}$, and hence the integrated expression may be written—

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

or

$$\frac{1}{a-x} - \frac{1}{a} = kt \text{ or } \frac{1}{t}\frac{x}{a(a-x)} = k.$$

The following data show the applicability of the above equation to the saponification[1] of ethyl acetate by NaOH, both these substances being present initially at the same equivalent concentration $a = \frac{N}{50}$, temp. 26° C.

Time t in Minutes.	$(a - x)$ = amount of NaOH not yet transformed, as given by the c.c. of $\frac{N}{8}$ oxalic acid required for the titration of 100 c.c. removed from the solution at time t. (The value assigned to a must be expressed in the same units.)	k.
5	10·24	5·625
15	6·13	5·37
25	4·32	5·405
35	3·41	5·27
55	2·31	5·385
120	1·10	5·645
		Mean 5·45

The constancy of k is fairly evident throughout.

It is not necessary, however, to start with equivalent amounts of the two substances in a bimolecular reaction. Suppose the initial quantity of ethyl acetate $= a$ and the initial quantity of alkali $= b$ in the given reaction; further if x is the amount transformed at time t, *i.e.* number of moles of each transformed (for the disappearance of one mole of ester necessarily entails the disappearance of one mole of alkali, as is evident from the stoicheiometric equation), the velocity expression is—

$$\frac{dx}{dt} = k(a-x)(b-x)$$

---

[1] Warder, *Ber.*, 14, 1361, 1881.

and on integration this becomes—

$$\frac{1}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}=k.$$

If one of the reactants—say that to which a refers, is present in very large excess, as is the case in the action of water on sugar during its inversion, we can neglect its change in concentration during the reaction, *i.e.* we can neglect x and b likewise compared to a. The above equation then becomes—

$$\frac{1}{ta}\log\frac{ba}{a(b-x)}\text{ or }\frac{1}{ta}\log\frac{b}{b-x}=k$$

and since a is necessarily constant—being simply the initial arbitrarily chosen concentration of water—we can rewrite the equation in the form—

$$\frac{1}{t}\log\frac{b}{b-x}=k_1$$

which is evidently identical with the monomolecular velocity expression previously obtained for such a case. An interesting instance of a "bimolecular reaction" is to be found in the rate of recombination of the ions (oppositely electrified particles) in a gas which has been subjected to some ionising agency, such as radium rays or ultraviolet light, and then removed from the action of the ionising agency. What happens is that one positive particle unites with one negative particle to give once more two neutral gas molecules. The work of Rutherford, Townsend, and others has shown that the following expression holds good:—

$$\frac{1}{N}-\frac{1}{N_0}=kt$$

where N is the number of ions in the gas after a time t, N_0 the number of ions originally present in the gas, and k is a constant known as the coefficient of recombination of the gas. If we write $N_0 = a$ and $N = (a - x)$ the above expression simplifies down to the one for a bimolecular reaction in which equivalent quantities of the reactants are present.

Termolecular Reactions.—The reaction of this type may be represented by any one of the following stoicheiometric equations:—

$$1A + 1B + 1C \rightarrow \text{one or more resultants.}$$
$$2A + 1B \rightarrow \quad " \quad " \quad "$$
$$3A \rightarrow \quad " \quad " \quad "$$

The differential equation corresponding to the first case in which all the substances are present at different initial concentrations a, b, c, will be—

$$\frac{dx}{dt}=k(a-x)(b-x)(c-x).$$

In the case of the second type of stoicheiometric equation, or in the first type in which $a = c$, we have the velocity equation—

$$\frac{dx}{dt} = k(a - x)^2(b - x).$$

In the case of the third type of stoicheiometric equation, or in the other two types, provided the initial concentrations are the same, that is, $a = b = c$, we find that the velocity equation is—

$$\frac{dx}{dt} = k(a - x)^3.$$

Let us integrate this simplest form—

$$\frac{dx}{dt} = -\frac{d(a - x)}{dt}$$

$$\therefore \frac{-d(a - x)}{(a - x)^3} = kdt$$

or $$+\tfrac{1}{2}(a - x)^{-2} = kt + \text{integration constant.}$$

When $t = 0$ $x = 0$, and the integration constant $= \frac{1}{2a^2}$, and hence the integrated form may be written—

$$\frac{1}{t} \cdot \frac{1}{2}\left\{\frac{1}{(a - x)^2} - \frac{1}{a^2}\right\} = k$$

This equation may be illustrated by the polymerisation of cyanic acid into cyamelide (van 't Hoff, *Études*, 90, 1884) and by the interaction of ferrous chloride, potassium chlorate, and hydrochloric acid investigated by Noyes and Wason (*Zeit. physik. Chem.*, **22**, 210, 1897).

Quadrimolecular Reactions.—There are only a few of such reactions known. The most general type of reaction velocity equation for four substances at different initial concentrations a, b, c, d, is—

$$\frac{dx}{dt} = k(a - x)(b - x)(c - x)(d - x).$$

The simplest case is that in which the initial concentrations are identical, *viz.*, $a = b = c = d$.

Thus $$\frac{dx}{dt} = k(a - x)^4$$

and on integration—

$$\frac{1}{t} \cdot \frac{1}{3}\left\{\frac{1}{(a - x)^3} - \frac{1}{a^3}\right\} = k.$$

By way of illustration, we may take the case of the reaction between HBr and $HBrO_3$, which was found to give a constant belonging to the quadri-molecular order (Judson and Walker, *Trans. Chem. Soc.*, **73**, 410, 1898). In aqueous solution at 25° the following data are given :—

t in Minutes.		k.
2	Initially the volume = 100 c.c. containing 5 c.c. HBr solution 5 c.c. $HBrO_3$,,	0·000000117
4		0·000000115
6		0·000000111
8		0·000000112
10		0·000000109
15		0·000000110
20		0·000000111
30		0·000000115
60		0·000000115

The conclusion arrived at was that the reaction was an ionic one—

$$2H^{\cdot} + Br' + BrO_3' \rightarrow HBrO + HBrO_2$$

(the substances on the right-hand side being both practically undissociated). This was borne out by the fact that when the reaction was carried out in fairly strong sulphuric acid, *i.e.* in large excess of $H^{\cdot}$, the reaction became apparently bimolecular, *i.e.* the $[H^{\cdot}]$ term is constant, and therefore the reaction may be written—

$$Br' + BrO_3' \rightarrow HBrO + HBrO_2.$$

Compare this case with that of the inversion of cane sugar in which a bimolecular reaction gives a monomolecular constant.

Quinquemolecular Reactions.—The only example of this type is that furnished by the reaction between potassium ferricyanide and potassium iodide (Donnan and Le Rossignol, *Trans. Chem. Soc.*, **83**, 703, 1903). We shall consider this later when we come to the question of determining the *order* of a reaction. [It should be mentioned, however, that Just (*Zeitsch. physik. Chem.*, **63**, 513, 1908) has reinvestigated the problem, introducing E.M.F. measurements as well as velocity measurements, and has come to the conclusion that this reaction is trimolecular, *i.e.* monomolecular with respect to potassium ferricyanide and bimolecular with respect to potassium iodide.]

Reaction of the Eighth Order.—R. Luther and F. H. McDougall (*Zeitsch. physik. Chem.*, **62**, 199, 1908) have investigated the action of HCl on $HClO_3$ in aqueous solution. When the chlorion (Cl′) content is not too great the stoicheiometric equation is—

$$4H^{\cdot} + 2ClO_3' + 2Cl' \rightarrow 2ClO_2 + Cl_2 + 2H_2O.$$

The velocity measurements showed that the chief reaction occurring was—

$$4H^{\cdot} + 2ClO_3' + 2Cl' \rightarrow \underset{\substack{\text{hypochloric acid} \\ \text{(not isolated)}}}{2H_2ClO_3} + Cl_2$$

i.e. an eighth-power reaction on the left-hand side. As a matter of fact, an equilibrium is finally set up, owing to the opposing reactions, examples of which will be studied later. (The *order* of the reaction was determined by van 't Hoff's method of varying the initial concentration and measuring the initial velocity.)

Comparison of Stoicheiometric Equations and Velocity Equations.—It must be noted that frequently the stoicheiometric equation does not necessarily correspond to the velocity equation. In general the velocity equation is of a simpler type. This is shown by the fact that there are numerous mono- and bimolecular reactions known, that is to say, using the corresponding velocity constant as the *criterion*, we find very many instances of reactions which yield good constant values for these simpler types. The instances of termolecular reactions are more scarce, the quadrimolecular still more rare, and so on. On the other hand, many stoicheiometric equations involve a large number of molecules. Take as an example the decomposition of phosphine, PH_3. Stoicheiometrically we represent this reaction by the equation—

$$4PH_3 \rightarrow P_4 + 6H_2$$

P_4 being the constitution of the phosphorus molecule. Instead of this reaction giving a quadrimolecular constant, it gives a monomolecular one, as is shown in the table below (König, *Zeitsch. physik. Chem.*, **12**, 155, 1892).

t in Hours.	Pressure of Gaseous Mixture.	k Calculated as Monomolecular Constant.	k Calculated as Quadrimolecular Constant.
0	715·21 mm.	—	—
7·83	730·13 ,,	0·00236	0·0173
24·17	759·45 ,,	0·00237	0·0201
41·25	786·61 ,,	0·00235	0·0229
63·17	819·96 ,,	0·00238	0·0288
89·67	855·50 ,,	0·00241	0·0385

The fact that a monomolecular constant is obtained suggests that the reaction goes in two stages, namely—

$$1PH_3 \rightarrow P + 3H$$

followed by

$$4P = P_4$$
$$2H = H_2$$

these being extremely rapid compared to the first.

For it is evident that it is the slowest reaction in a series which will determine the resultant velocity of the whole.

[For an alternative and not unlikely explanation of the above phosphine case, *cf.* Mellor, *Statics and Dynamics*, p. 57. Whichever explanation is correct does not, however, affect the distinction which in many cases must be drawn between stoicheiometric molecular numbers and velocity molecular numbers.]

The Characteristic Distinctions between Reactions of Different Orders.

—The simplest velocity equations characteristic of reactions of different orders are, as we have already seen—

For monomolecular reactions $\frac{1}{t}\log\frac{a}{a-x} = k.$

$$\left.\begin{array}{l}\text{For bimolecular reactions}\\ \\ \text{For termolecular reactions}\end{array}\right.\left\{\begin{array}{c}\text{Equivalent}\\ \text{quantities}\\ \text{being}\\ \text{present}\\ \text{initially}\end{array}\right\}\begin{array}{l}\frac{1}{t}\cdot\frac{x}{a(a-x)} = k\\ \\ \frac{1}{t}\cdot\frac{1}{2}\left\{\frac{1}{(a-x)^2}-\frac{1}{a^2}\right\} = k\end{array}$$

and so on.

These expressions are sufficiently different from one another, as a rule, though not always, that if one of them represents the reaction under investigation, the others cannot, *i.e.* the others will give inconstant values for k.

Now let us consider the question of the time taken to decompose one-half of the original substance, and see how this time varies in the different orders. We are considering the instant at which $x = \frac{a}{2}$. On substituting this value in the monomolecular type we obtain the expression $\frac{1}{t}\log 2 = k$. Log 2 is of course a constant itself, and hence we find that the value of t is a constant, being expressible simply in terms of log 2 and k. This means that t—where t is the time required for half decomposition of the substance—is independent of the value of a. That is, if we start with a 1 normal solution of a substance or with a $\frac{N}{10}$ solution of the same substance, the time taken for half of the substance to be decomposed in each case is the same. Now take a bimolecular reaction (in which as a simplification we assume equivalent initial amounts of both substances).

When $x = \frac{a}{2}$ the bimolecular expression becomes—

$$\frac{1}{t}\cdot\frac{\frac{a}{2}}{a\cdot\frac{a}{2}} = k \text{ or } \frac{1}{t}\cdot\frac{1}{a} = k.$$

That is, the time required for half decomposition is *not* independent of a, the initial concentration of the reacting substances. As one sees, t is inversely proportional to a. Thus, if we start with $\frac{N}{1}$ and $\frac{N}{10}$ solutions, respectively, of the reacting mixture, the time taken for the reaction to proceed to the one-half stage is different in the two cases. In fact, the time of half decomposition in the case of the normal initial concentration will be one-tenth of the time taken for half decomposition in the case of the $\frac{N}{10}$ solution. Again, in the case of termolecular reactions, we see on substituting $x = \frac{a}{2}$ that the time t is inversely as the square of the initial concentration, and that in general for an n molecular reaction the time ($t_{\frac{1}{2}}$) required for half decomposition is inversely proportional to the ($n - 1$) power of the initial concentration (each component being assumed present initially at equivalent concentrations). Hence in general we may write—

$$t_{\frac{1}{2}\text{ decomposition}} \propto \frac{1}{a^{n-1}}.$$

These considerations. lead us naturally to take up the question: To what order does a given reaction belong? for we have seen that the stoicheiometric equation itself is not always identical with the velocity equation which determines the reaction.

METHODS OF FINDING THE NUMBER OF MOLECULES PARTICIPATING IN A REACTION.

A. The most direct method is to measure the rate of the reaction by suitable means at given intervals of time, and simply work out the values of k, which are given by the different expressions for mono-, bi-, termolecular reactions, and the order which gives the most constant value for k is the order assigned to the reaction. This method is unsatisfactory when complicating side reactions occur—to which we shall come shortly.

B. We may introduce the ideas with which we were dealing, when it was shown that the time of half decomposition was $\propto \frac{1}{a^{n-1}}$. Suppose we take a reaction and make measurements using two different initial concentrations a_1 and a_2. Then if t_1 and t_2 are the times of half decomposition in each case—

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}.$$

From which n can be obtained.

This method, however, may be made more useful by being generalised as follows. Consider the intervals of time t_1 and t_2 (for the same reaction) required for the transformation of the same fractional part (not necessarily one half) of the original substance, and carry out the same process of reasoning as before. Thus suppose we denote the fractional amount transformed by ϕ. That is to say, if in two experiments a_1 and a_2 denote the initial concentrations of the reacting bodies, then let t_1 and t_2 denote the respective intervals of time in which x has reached the values ϕa_1 and ϕa_2 in each instance. It may be easily seen that if the reaction is monomolecular, and the term ϕa be introduced instead of x, we find t independent of a. If the reaction is bimolecular, we find that t is inversely as a, and so on. In fact, we find the same expression as before, *viz.*—

$$t \propto \frac{1}{a^{n-1}}.$$

Hence, applying this expression to the two cases mentioned, we obtain—

$$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}}$$

or

$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}}.$$

C. Van 't Hoff's differential method is less accurate than the foregoing, and need not be discussed at length: *cf.* Mellor's *Statics and Dynamics*, p. 59.

D. *Ostwald's Isolation Method.*—This method really involves the artificial simplification of a reaction, *i.e.* the lowering of its order by the use in turn of a large excess of all components except one. The mode of reaction of each is thus determined separately.

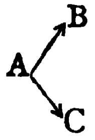
Having now discussed the various types of reaction velocities in relation to isolated reactions, *i.e.* those which are not complicated by additional reactions, it is necessary to take up the question of several reactions occurring at the same time. These are known as *simultaneous reactions.*

2. *Simultaneous Reactions.*

When several reactions occur at the same time in a given system we are dealing with simultaneous reactions. These may be divided into three classes:—

(1) Side reactions.
(2) Consecutive reactions.
(3) Opposing reactions.

A side reaction is one in which a reactant gives rise to more than one independent resultant, *e.g.*



in which B and C may not have any chemical affinity for one another.

Consecutive reactions may be represented by the scheme

$$A \rightarrow B \rightarrow C.$$

Opposing reactions are those in which the reaction does not go to an end, but an equilibrium is reached of the type dealt with at length in considering homogeneous equilibrium, *e.g.*—

$$A \rightleftarrows B.$$

We shall consider these three classes of simultaneous reactions in turn.

A. Side Reactions.

In the case represented by—

$$\begin{tikzcd} & mB \\ nA \arrow[ur] \arrow[dr] & \\ & (n-m)C \end{tikzcd}$$

$+ \frac{dx}{dt}$ will be the rate of formation of both B and C observed together.

$- \frac{dx}{dt}$ denotes the rate of disappearance of A.

$+ \frac{dy}{dt}$ „ „ appearance of B.

$+ \frac{dz}{dt}$ „ „ „ „ C.

Then we have at any moment the relation—

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt}.$$

Suppose we consider monomolecular reactions, *i.e.*—

$$\begin{cases} 1A \rightarrow 1B \\ 1A \rightarrow 1C \end{cases}$$

then $\frac{dy}{dt} = k_1(a - x)$, where a is the original amount of A, and x is the amount of A transformed at the moment in question.

Similarly $$\frac{dz}{dt} = k_2(a - x).$$

$$\therefore \frac{dx}{dt} = k_1(a - x) + k_2(a - x) = (k_1 + k_2)(a - x)$$

which gives on integration—

$$\frac{1}{t} \log \frac{a}{a - x} = k_1 + k_2 = K \text{ say} \quad . \quad . \quad . \quad (1)$$

Now to evaluate k_1 and k_2 separately we must know some other connection between them. This connection appears if we remember that the rate of formation of B or C at any moment is the product of the respective velocity coefficients k_1 or k_2 into the amount of the original substance $(a - x)$ present. But $(a - x)$ is the same for each side reaction. So that the ratio of rate of formation of B to that of C, or what is the same thing, the ratio of the amount of B formed at any moment to the amount of C at the same moment, is simply the ratio of the velocity coefficients. That is—

$$\frac{\text{Amount of B at any stage}}{\text{Amount of C at the same stage}} = \frac{k_1(a - x)}{k_2(a - x)} = \frac{k_1}{k_2} = \text{L}.$$

We can take as the most convenient stage the end of the reaction, and estimate the relative amounts of B and C formed, the ratio giving us $\frac{k_1}{k_2} = \text{L}$. With this information we can now obtain k_1 and k_2 separately with the aid of equation (1). For evidently—

$$k_1 = \frac{\text{KL}}{\text{L} + 1} \qquad k_2 = \frac{\text{K}}{\text{L} + 1}$$

and K and L are directly measurable quantities.

Holleman (*Zeitsch. physik. Chem.*, **31**, 79, 1899) showed that the nitration of benzoic acid with excess of nitric acid, resulted in the formation of *o*-, *m*-, and *p*-nitro-benzoic acids as monomolecular side reactions.

Reactions of higher orders may be treated in a similar manner.

Wegscheider's Test for Side Reactions (distinguishing them from Consecutive or Opposing Reactions).—We have really introduced Wegscheider's principle in the evaluation of the ratio $\frac{k_1}{k_2} = \text{L}$. It is: *The ratio between the amount of the substances formed in two side reactions is independent of the time.*

For monomolecular side reactions—

$$i.e.\ \text{simultaneously} \begin{cases} 1\text{A} \rightarrow \text{B} \\ 1\text{A} \rightarrow \text{C}. \end{cases}$$

$$\text{Rate of formation of B} = \frac{d\text{B}}{dt} = k_1[\text{A}].$$

$$\text{,,} \quad \text{,,} \quad \text{,,} \quad \text{C} = \frac{d\text{C}}{dt} = k_2[\text{A}].$$

$$\therefore \frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} \text{ or } \frac{\text{quantity of B present at any time}}{\text{quantity of C present at any time}}$$

$$= \frac{k_1[\text{A}]}{k_2[\text{A}]} = \text{constant L independent of time.}$$

Similarly for polymolecular side reactions, ***each of which involves the same number of* A *molecules***, we have—

$$\frac{dB}{dt} = k_1[A]^n$$

$$\frac{dC}{dt} = k_2[A]^n$$

and $\dfrac{\text{Amount of B formed}}{\text{Amount of C formed}} = \dfrac{k_1[A]^n}{k_2[A]^n} =$ constant independent of time.

Note, however, that for side reactions which do *not* involve the same number of molecules of A, *i.e.* $\begin{cases} nA \rightarrow B \\ mA \rightarrow C \end{cases}$

then $$\frac{dB}{dt} = k_1[A]^n \qquad \frac{dC}{dt} = k_2[A]^m$$

and hence—

$$\frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} = \frac{\text{quantity of B present at any moment}}{\text{quantity of C present at any moment}}$$

$$= \frac{k_1}{k_2}[A]^{n-m}$$

which is dependent on time since the symbol [A] denotes concentration of A which varies with the time. Hence Wegscheider's test has this limitation.

The utility of Wegscheider's method may be illustrated by the following example. Skraup showed that when a strong acid—such as hydrochloric acid—acts on cinchonine it forms cinchonine hydrochloride, and at the same time an isomeric form of cinchonine hydrochloride (the isomerism of course exists in the cinchonine residue). Skraup considered that the reactions are consecutive, the ordinary hydrochloride being first formed, and the isomeric form being produced from this in turn. Wegscheider pointed out, however, that the quantities of ordinary hydrochloride and its isomer were in constant ratio to one another, independent of the time chosen for measurement. Hence the reactions must be side reactions and not consecutive.

They may be represented therefore by—

$$\text{Cinchonine} + \text{HCl} \begin{array}{l} \nearrow \text{Cinchonine hydrochloride} \\ \\ \searrow \text{Isomeric cinchonine hydrochloride} \end{array}$$

or more accurately—

$$\begin{array}{lclll} n \text{ cinchonine} & \rightarrow & n_1 \text{ cinchonine-HCl} \\ n \quad \text{,,} & \rightarrow & n_1 \text{ iso} \quad \text{,,} \quad \text{,,} \end{array}$$

where n appears actually to be unity in this case.

Note that if it had required a *different* number of cinchonine molecules to form the normal hydrochloride and iso-hydrochloride respectively, the reactions might still have been side reactions, but

Wegscheider's test would have failed. A further instance of the applicability of Wegscheider's method is found in the monomolecular decomposition of camphor carboxylic acid $C_{10}H_{15}O.COOH \rightarrow C_{10}H_{16}O + CO_2$. In addition to this reaction the acid, in alcoholic solution, undergoes *esterification* at the same time with practically the same speed. The results obtained by Bredig and Balcom (*Ber.*, **41**, 740, 1908) support Wegscheider's principle very completely.

B. Consecutive (Simultaneous) Reactions.

An important principle to be remembered in connection with consecutive reactions is that, in a series of reactions occurring consecutively, the slowest one determines the order of the reaction. In fact, if one reaction of the series is very slow compared to the others, we may even fail to detect the presence of these others, at least by velocity constant measurements. We have already found such an instance in the dissociation of phosphine PH_3, which instead of involving four molecules only involves one, the main (slow) reaction being $PH_3 \rightarrow P + 3H$ followed by the much faster formation of the respective molecules P_4 and H_2 from the atoms. There are a number of reactions, however, which show by certain abnormalities in the velocity constant (when one attempts to fit results to some of the simple velocity equations) that consecutive changes are in operation. The general treatment of such cases—which unfortunately cannot go far owing to mathematical difficulties—may be illustrated by the simplest case, namely, the two consecutive monomolecular reactions $1A \rightarrow 1B \rightarrow 1C$.

Starting with a mols of A, suppose that after a time t, there are now x mols of A remaining, and y mols of B and z mols of C are now in existence. The first relation we have is—

$$x + y + z = a \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Also the rate of disappearance of A, namely $-\frac{dx}{dt}$, is given as usual by the relation—

$$-\frac{dx}{dt} = k_1x \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_1 is the velocity constant of transformation of A into B. The rate of formation of C is—

$$+\frac{dz}{dt} = k_2y \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where y is the concentration of B at the time t, C being formed from B with the velocity coefficient k_2. Now the rate at which B accumulates in the system is evidently the difference between the rate of its formation from A (namely $-\frac{dx}{dt}$, where $-\frac{dx}{dt} = k_1x$) and its own rate of transformation into C, namely $\frac{dz}{dt} = k_2y$. Hence—

$$\frac{dy}{dt} = -\frac{dx}{dt} - \left(+\frac{dz}{dt}\right) = -\frac{dx}{dt} - \frac{dz}{dt} \quad . \quad . \quad . \quad (4)$$
$$= k_1x - k_2y$$

From the four relations given it is found on integration that $x + y$, *i.e.* the amount of A left in the system + the actual amount of B present at time t, or what is the same thing, the expression $a - z$, is given by the relation—

$$z - a = a\left(\frac{k_2}{k_1 - k_2}e^{-k_1t} + \frac{k_1}{k_2 - k_1}e^{-k_2t}\right) \quad . \quad . \quad (5)$$

where we have written x in the form ae^{-k_1t}. For certain mathematical reasons (for which see Mellor, *ibid.*, p. 98) the above expression cannot be rigidly tested in actual cases unless we know k_1 and k_2 separately. It may be illustrated—though the actual mathematical calculations were not actually carried out by using the above formula, owing to the rather complicated nature of the reaction—by the reaction between potassium persulphate and phosphorous acid in the presence of hydriodic acid. Without the HI the reaction, which is then an exceedingly slow one, is represented by—

$$H_3PO_3 + K_2S_2O_8 + H_2O \rightarrow K_2SO_4 + H_2SO_4 + H_3PO_4$$

In the presence of HI, however, the solution is seen to go brown, evidently due to the formation of iodine. The total reaction is then believed to be composed of two parts in succession—

$$\text{(I)}\ K_2S_2O_8 + 2HI \rightarrow K_2SO_4 + H_2SO_4 + I_2$$
$$\text{(II)}\ H_3PO_3 + I_2 + H_2O \rightarrow H_3PO_4 + 2HI$$

The sum of the two is evidently identical with the previous one as far as final products are concerned. Now equation (1) was investigated by itself by Price (*Zeitsch. physik. Chem.*, **27**, 476, 1898), the velocity constant being 0·0065. This reaction corresponds to the disappearance of A in the preceding theoretical discussion and $k_1 = 0·0065$. Reaction (II) has also been investigated, this corresponding to the formation of the body C and $k_2 = 0·157$. The total reaction has been investigated by Federlin (*Zeitsch. physik. Chem.*, **41**, 565, 1902), and the following table contains some of his results :—

t Hours.	Iodine.		Persulphate.	
	Observed.	Calculated.	Observed.	Calculated.
0·5	4·55	3·44	8·08	9·13
1·0	5·39	4·58	4·89	6·72
1·5	5·05	4·84	3·13	4·98
2·0	4·18	4·64	2·17	3·64
2·5	3·38	4·22	1·49	2·68
3·0	2·59	3·68	1·01	1·94

Note that the iodine goes through a maximum. The shape of the curves shown on the diagram (Fig. 54) is very characteristic of consecutive reactions.

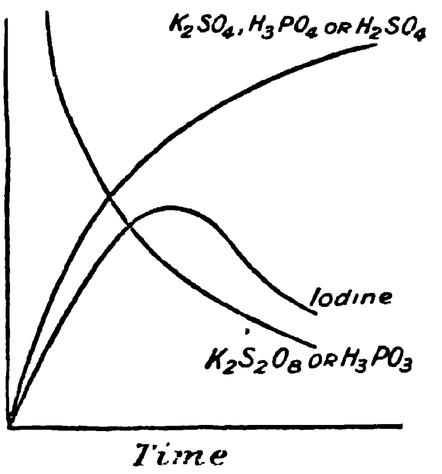


FIG. 54.

Another example of consecutive reactions is afforded by the saponification of dicarboxylic esters, such as ethyl succinate by alkali. If the reaction is treated as a bimolecular one, we find that the "constant" will fall to less than half its initial value. The mechanism, therefore, seems to be, that there are two reactions in succession.

(1) The formation of ethyl sodium succinate.

(2) The saponification of ethyl sodium succinate. For details, which are rather scanty, *cf.* Mellor, pp. 101 *seq.*

Probably the most interesting types of consecutive reactions are to be found in radioactive changes, as already mentioned. These strictly belong to *heterogeneous* reaction velocities, but may be considered here. We are here dealing with a long series of consecutive changes. If we look upon the expulsion of α rays (which when deprived of their charge are identical with helium), or if we regard the expulsion of β and γ rays as "chemical" reactions, we are here furnished with side reactions accompanying the consecutive changes. To illustrate in a general way how the existence of such consecutive changes was indicated by abnormalities in the decay curves, we may take the case of isolated thorium X, which gives rise to thorium emanation (Rutherford and Soddy, *Trans. Chem. Soc.*, **81**, 837, 1898). A piece of platinum wire upon which was deposited some thorium X was seen to lose its activity (as measured by its capability of discharging an electroscope), the following figures indicating the rate. The initial activity is called 100.

Time in days.	Activity of Th X.
0	100
1	117
2	100
3	88
4	72
6	53
9	29·5
10	25·2
13	15·2
15	11·1

These data are plotted in the following diagram (Fig. 55*a*). It will be observed that a maximum is passed through in the region of the first day interval. This suggests that at least *one* new radioactive product has been formed from the thorium X. This has been identified as thorium emanation. The shape of the curve should be compared with that of the production of iodine obtained in the case of the action of $K_2S_2O_8$ on H_3PO_3 in presence of HI (Fig. 54). By means of the systematic examination of the decay curves of various products in turn, other radioactive changes can be detected. *Cf.* Fig. 55*b*, which illustrates the recovery of activity of radium salt (curve A) and simultaneously the decay of radium emanation (curve B). These combined produced a "humped" curve (Rutherford and Soddy, *Phil. Mag.*, [6], **5**, 455, 1903). A curve which shows several humps points to the existence of, at least, a corresponding number of radioactive substances.

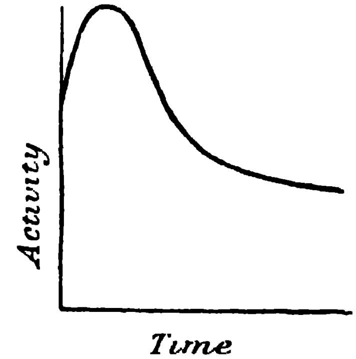


FIG. 55*a*.

Initial Disturbance and Period of Induction.—These points may be raised at this juncture, since they are generally due to consecutive reactions, though there are other causes known which in certain cases will account for them. Any abnormality—such as that of variation in the velocity constant—which occurs in the earliest stages of a reaction, is called in general an initial disturbance. A period of induction is a particular type of initial disturbance in which we find that the combination or decomposition of a certain substance is delayed for a short period of time. That is to say, the velocity curve, instead of falling steadily, remains horizontal for a time, and then becomes normal in behaviour. The phenomenon of induction period was first observed by Cruikshank in 1801, who noted that the combination of hydrogen and chlorine did not proceed very rapidly until the mixture had been exposed

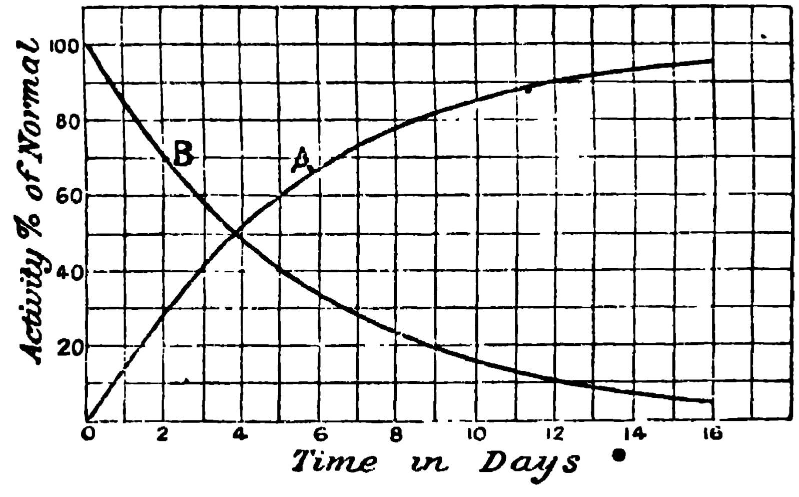


FIG. 55*b*.

to the light for some time. Bunsen and Roscoe named this stage of retardation in velocity the period of induction. Such abnormality may be ascribed roughly to three causes—

(1) Presence of consecutive reactions.

(2) The existence of passive resistances, *i.e.* something which prevents the reaction starting off at full speed, but about which we know nothing, the term being simply an expression for lack of information.

(3) Autocatalysis, which we shall consider later on, in discussing homogeneous catalysis in general.

C. Opposing Reactions.

Opposing reactions result in chemical equilibrium, as determined by the law of mass action. We have already discussed the question of such equilibrium in homogeneous systems at considerable length. It will be remembered that the equilibrium constant K is simply the ratio of the velocity constants k_1 and k_2 of the opposing reactions. It will also be remembered that in dealing with the indirect method of determining K it was stated that K might be determined by measuring k_1 and k_2 for each reaction at a very early stage in each case, in fact the so-called initial velocity stage. Thus, if we take the familiar reaction—

$$CH_3.COOC_2H_5 + H_2O \leftrightarrows CH_3.COOH + C_2H_5.OH$$

(*hydrochloric acid being used as a catalyst*) and use Knoblauch's data (*Zeitsch. physik. Chem.*, **22**, 268, 1897), we find, starting with ester and water, the following data. Experiments carried out at 25° C.

t Minutes.	Quantity of Acid Formed.	$\frac{\delta \text{ Acid}}{\delta t}$.
0	0·0	—
78	0·0777	0·000996
86	0·0862	0·001003
94	0·0930	0·000989
		Mean = 0·000996

Similarly starting with acid and alcohol.

t Minutes.	Quantity of Ester Formed.	$\frac{\delta \text{ Ester}}{\delta t}$.
0	0	—
44	0·1327	0·00302
53	0·1628	0·00307
62	0·1847	0·00298
		Mean = 0·00303

The ester + water solution was prepared so as to contain 1 mol of ethyl acetate + 12·215 mols of water in a liter.

The initial velocity constant k_1 of acid and alcohol formation is then given by the expression—

$$\frac{dx}{dt} = k_1 \times \text{initial } C_{\text{ester}} \times \text{initial } C_{\text{water}}$$

$$\begin{aligned} \text{or} \qquad 0{\cdot}000966 &= k_1 \times 1 \times 12{\cdot}215 \\ \therefore k_1 &= 0{\cdot}0000815 \\ \text{and} \qquad k_2 &= 0{\cdot}000238 \end{aligned}$$

and hence $$\frac{k_2}{k_1} = \text{K} = 2{\cdot}92$$

$$\text{K observed} = 2{\cdot}84 \text{ (after 24 hours)}$$

(possibly too short a time).

Knoblauch points out that Berthelot's value for K is 4 (over a fairly wide temperature range in the absence of hydrochloric acid), and ascribes the difference from his own as due to the hydrochloric acid; see, however, the later work of Jones and Lapworth (*Trans. Chem. Soc.*, **99**, 1427, 1911) on the "removal" of water from the system by the hydrochloric acid, already discussed in dealing with homogeneous equilibrium, thereby giving values for K *higher* than 4.

The above method cannot, however, be strictly accurate, for at any stage of the reaction—and therefore, of course, even at the earliest—the correct expression for the rate of change is—

$$\frac{dx}{dt} = k_1(a - x)(b - x) - k_2x^2$$

where a and b are the original amounts of ester and water present, and hence the rate of decrease of ester, for example, is not characterised by a factor k_1, but by $(k_1 - k_2)$.

For the present, instead of further studying these bimolecular and opposing reactions, let us consider an example of two opposing monomolecular reactions, namely, the conversion of hydroxybutyric acid into the corresponding lactone. This is carried out in solution in the presence of H˙ ions as catalyst; the H˙ ions at the same time cause the hydroxybutyric acid to assume a practically unionised state. The reaction velocity is thus—

$$\frac{dx}{dt} = k_1(a - x) - k_2x$$

where a is the initial amount of hydroxybutyric acid, and x the quantity transformed into lactone at the time t.

If the equilibrium constant is K—

$$\text{K} = \frac{k_1}{k_2}.$$

Then
$$\frac{dx}{dt} = k_2\{Ka - x(K+1)\}$$
$$= k_2(K+1)\left(\frac{Ka}{K+1} - x\right)$$

and since
$$\frac{dx}{dt} = \frac{-d\left(\frac{Ka}{K+1} - x\right)}{dt}$$

$$\therefore \frac{-d\left(\frac{Ka}{K+1} - x\right)}{\left(\frac{Ka}{K+1} - x\right)} = k_2(K+1)dt \text{ or } (k_1 + k_2)dt$$

and hence on integrating—
$$-\log\left(\frac{Ka}{K+1} - x\right) = (k_1 + k_2)t + \text{constant}$$

$$\text{where } t = 0 \quad x = 0 \quad \therefore \text{constant} = -\log\frac{Ka}{K+1}$$

$$\therefore \frac{1}{t}\log\frac{\frac{Ka}{K+1}}{\frac{Ka}{K+1} - x} = k_1 + k_2$$

or
$$k_1 + k_2 = \frac{1}{t}\log\frac{Ka}{Ka - (K+1)x}.$$

This expression was verified by Henry as follows:—

K (found) at 25° C. = 2·68

t Minutes.	x.	Value of $\frac{1}{t}\log\frac{Ka}{Ka-(K+1)x}$.
21	2·39	0·0411
50	4·98	0·0408
80	7·14	0·0444
120	8·88	0·0400
220	11·56	0·0404
320	12·57	0·0398
47 hours {equilibrium reached	13·28 {used for K calculation	—

Another example of monomolecular opposed reactions is to be found, in adding a small quantity of acetic acid to a concentrated solution of water and alcohol, whereby, of course, ethyl acetate is formed, but the alcohol and water concentration may be regarded as constant, so that the reaction is virtually acid $\rightleftarrows$ ester, and the equation is—

$$\frac{dx}{dt} = k(a - x) - k'x_2$$

where a is the amount of acid present initially, and x is the amount transformed into ester.

The same reaction, as already pointed out, is bimolecular, when no component is present in excess. Thus, if 1 mol of ester + 1 mol of water are present to start with, then at time t—

$$\frac{dx}{dt} = k_1(1 - x)^2 - k_2x^2$$

and $$\frac{k_1}{k_2} = \frac{1}{4} \text{(Berthelot and Pean de St. Gilles)}$$

so that on integration we obtain—

$$\tfrac{4}{3}(k_1 - k_2) = \frac{1}{t} \log \frac{2 - x}{2 - 3x}.$$

This equation is found to agree with facts, *i.e.* the right-hand side of the equation does really give a constant, *viz.* $\{\tfrac{4}{3}(k_1 - k_2)\}$. Knowing $k_1 - k_2$ and also $\frac{k_1}{k_2}$, it is easy to determine k_1 and k_2 separately.

EFFECT OF TEMPERATURE ON VELOCITY.

From the kinetic standpoint of reaction velocities we might expect that the rate of reaction would depend on the number of collisions between the molecules in unit time, and hence if we could calculate from the kinetic theory the increase in collisions per degree rise in temperature, we would have obtained the value of the increase of the reaction velocity constant, due to temperature. The kinetic theory of gases leads to the following expression (Meyer, *Kinetic Theory of Gases*, translated by Baynes, p. 168):—

$$\text{Frequency of collision} = \left(1 + \frac{c}{T}\right)\sqrt{2}\pi s^2\frac{\Omega}{\lambda^3}$$

where πs^2 is the cross-section of the molecular sphere of action, Ω is the arithmetical mean molecular speed (a quantity which differs slightly as far as numerical values are concerned from the root-mean-square velocity, which appears in the kinetic energy expressions which define the temperature of the system), λ^3 is the volume "region," which contains one molecule. The term $\left(1 + \frac{c}{T}\right)$ takes into account the cohesive forces existing between the molecules. Now the term $\left(1 + \frac{c}{T}\right)$ decreases as the temperature rises, and Ω increases as the temperature increases, so that on the whole the frequency of collision may or may not increase with temperature. Let us consider, however, the limiting case, *i.e.* the maximum variation in collisions to be expected by change in temperature. This can be accomplished by omitting the cohesion term, and making frequency $\propto$ T. On this assumption one can easily see that if we raise the temperature from 273° abs. to 283° abs., we increase the number of collisions per second to the extent of 2 per cent. But it has been found that, as a very approximate average, a rise of 10° causes the reaction velocity to double or treble itself, *i.e.* an increase of 100 per cent. to 200 per cent. It is therefore clear that some very large effect is coming in, which is not taken into account at all by the kinetic theory. Physical changes in general, such as viscosity, will not account for it. For this reason Arrhenius put forward the hypothesis of the existence of two types of molecules, active and passive, with an equilibrium existing between them. Let us take the case of cane sugar in water. The number of "active" molecules is supposed to be very small compared to the number of "passive" ones present. On raising the temperature, the equilibrium between these two kinds is supposed to shift over very rapidly, so that not only have we an increased collision frequency, but still more, we have a largely increased number of active molecules ready to take part in the reaction.

In connection with the effect of temperature on the equilibrium constant K of a reversible reaction, van 't Hoff deduced on thermodynamical grounds the following relation:—

$$\frac{d \log K}{dT} = \frac{Q}{RT^2}$$

where Q is the heat absorbed per gram-molecule in the reaction, R is the gas constant, and T the absolute temperature. Now K may be written $\frac{k_1}{k_2}$, where k_1 and k_2 are the velocity coefficients for the direct and reverse reactions. So that the van 't Hoff relation becomes—

$$\frac{d \log \frac{k_1}{k_2}}{dT} = \frac{Q}{RT^2}$$

and if we make the assumption that throughout the range of temperature investigated, Q is constant, we find on integration—

$$\log K_{T_2} - \log K_{T_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or

$$\log \left(\frac{k_1}{k_2}\right)_{T_2} - \log \left(\frac{k_1}{k_2}\right)_{T_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

This, however, only connects the difference of the logs of the ratios of the opposing velocity constants with the temperature. It does not give us the effect of temperature on the separate velocity constants, or on the velocity constant of an irreversible reaction, which goes practically to an end. It has been found, however, that the following empirical relation holds good (Arrhenius, *Zeitsch. physik. Chem.*, **4**, 226, 1889) for "irreversible" reactions at different temperatures, *viz.*—

$$k_{t_2} = k_{t_1} e^{A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

which is evidently—

$$\log \frac{k_{t_2}}{k_{t_1}} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right), \text{ where A is a constant.}$$

It thus bears a formal resemblance to the van 't Hoff equation for variations in the equilibrium K. By way of illustration of this, one may quote the results of Spohr (*Zeitsch. physik. Chem.*, **2**, 195, 1888) on the rate of inversion of cane sugar—

Temperature, Centigrade.	*k* Calculated.	A = 12,820. *k* Observed.
25	(9·67)	9·67
40	75·7	73·4
45	144	139
50	(268)	268
55	491	491

The following table illustrates the same expression applied to the case of the saponification of ethyl acetate by NaOH (Warder, *Amer. Chem. Journ.*, **3**, 203, 1881; *Ber. d. deutsch. Chem. Gesell.*, **14**, 1365, 1881):—

Temperature, Centigrade.	*k* Calculated.	A = 5579. *k* Observed.
3·6	1·48	1·42
5·5	1·70	1·68
7·2 = t_1	(1·92)	1·92
11·0	2·51	2·56
12·7	2·82	2·87
19·3	4·38	4·57
20·9	4·86	4·99
23·6	5·78	6·01
27·0	7·16	7·24
28·4	7·81	8·03
30·4	8·82	8·88
32·9	10·24	9·87
34·0 = t_2	(10·92)	10·92
35·0	11·60	11·69
37·7	13·59	13·41

Warder himself employed an empiric formula of a different type, which agreed with the data about as well as that given. Warder's formula may be put in the form—

$$k = A' + BT^2$$

i.e. the velocity constant is put proportional to the square of the absolute temperature.

Arrhenius has applied his hypothesis of active and passive molecules to show how one may arrive at the expression—

$$\log \frac{k_{t_2}}{k_{t_1}} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

It will be evident, however, that the "proof" does not rest on very solid ground.

Suppose we denote the equilibrium constant between active and passive molecules by the symbol X, then it follows as a particular case of the van 't Hoff theorem—

$$\frac{d \log X}{dT} = \frac{q}{RT^2}$$

where q denotes the heat absorbed in converting one gram mole from the passive into the active state. Let us assume that q is constant over a fairly wide temperature range. $\frac{q}{R}$ can then be written A, and on integrating—

$$\log \frac{X_{T_2}}{X_{T_1}} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \quad . \quad . \quad . \quad (1)$$

Note that A in this case contains q, the heat of transformation from inactive to active molecules. It has nothing to do with the heat of transformation Q involved in the further chemical reaction, say of cane sugar into dextrose + lævulose. The measurement of the heat of the reaction Q does not allow us to calculate the velocity constant, for the relation $\frac{d \log K}{dT} = \frac{Q}{RT^2}$, which is absolutely sound, has reference only to the ratio of *opposing* velocities, at different temperatures, as has been already pointed out.

The above expression (1) is open, however, to the following criticism.

Arrhenius assumes that in a solution (of sucrose, for example) the active molecules or "actives" only represent a very small fraction of the total sucrose molecules, equilibrium between them being defined by the mass action principle—

$$X = C_{\text{actives}} / C_{\text{passives}}.$$

Since C_{actives} is very small we can write as a close approximation, $C_{\text{passives}} = C_{\text{total sucrose}}$. Suppose we do this at two different temperatures T_1 and T_2. At T_1 the reaction velocity $\left(\frac{dx}{dt}\right)_{T_1}$ is proportional to the concentration of the "actives" in accordance with the principle of mass action. We have therefore—

$$\left(\frac{dx}{dt}\right)_{T_1} = h \, . \, C_{\text{actives}} = h \, . \, X_{T_1} \, . \, C_{\text{passives}} = h \, . \, X_{T_1} \, . \, C_{\text{total sucrose}},$$

where h is a proportionality constant or velocity constant not directly amenable to experimental measurement. In the ordinary way of writing the above reaction velocity equation we have

$$\left(\frac{dx}{dt}\right)_{T_1} = k_{T_1} \cdot C_{\text{total sucrose}},$$

where k_{T_1} is the *observed* velocity constant at the temperature T_1. Similarly at temperature T_2 we have—

$$\left(\frac{dx}{dt}\right)_{T_2} = h' \cdot X_{T_2} \cdot C_{\text{total sucrose}},$$

in which h' is a velocity constant analogous to h. Hence, if k_{T_2} is the *observed* velocity constant of the reaction at the higher temperature T_2 we have—

$$\left(\frac{dx}{dt}\right)_{T_2} = k_{T_2} \cdot C_{\text{total sucrose}}.$$

It follows from the above expressions that the ratio of the observed velocity constants at the two temperatures is given by—

$$\frac{k_{T_2}}{k_{T_1}} = \frac{h' \cdot X_{T_2}}{h \cdot X_{T_1}}$$

or

$$\log (k_{T_2}/k_{T_1}) = \log (h'/h) + \log (X_{T_2}/X_{T_1})$$

In order to arrive at Arrhenius's result, *viz.* $\log (k_{T_2}/k_{T_1}) = \log (X_{T_2}/X_{T_1})$ it is obviously necessary to assume that

$$h' = h.$$

This may be true, but it is by no means certain.

On the experimental side the chief support for Arrhenius's idea of active and passive molecules lies in the spectrometric observations of Baly and F. O. Rice (*Trans. Chem. Soc.*, **101**, 1475, 1912).

The principal criticism of the concept of active and passive molecules, having a real existence and existing in mass action equilibrium with each other, enters when the concept is extended to account for the catalytic influence of say $H^\cdot$ ions or other solutes, a subject which will be discussed in the next section. The concept of active and passive molecules has in fact been applied to cases of catalysis, the idea being that a catalyst, such as $H^\cdot$ ion, acts as an accelerator in virtue of the effect which it exerts on the number of active molecules, increasing these to a considerable extent, and thereby hastening the reaction. If this were true, we would have a case in which the equilibrium constant, X, was altered, and altered very considerably, by the presence of a dissolved catalyst. This is contrary to all experience in those cases in which equilibrium constants can be measured. It is therefore too uncertain to be accepted in a case in which we are unable to verify it experimentally. That mixed solvents, *i.e.* the addition of a considerable quantity of one solvent to another, can bring about a shift of the equilibrium constant is known; we have already discussed such a case in connection with Godlewski's determination of the Ostwald constant for certain weak acids in alcohol-water mixtures. This is, however, quite a different state of affairs from that represented by the addition of say H ions (in the form of an acid) in quite small quantities, so small, in fact, that the properties of the medium are only slightly altered.

As a matter of fact, it is quite possible to account not only for the marked effect of temperature in the case of a *monomolecular* reaction, but also for the effect of catalysts, on a purely physical basis, which does not require any explicit assumption regarding the equilibrium between active and passive molecules, but simply deals with the problem from the standpoint of the internal energy of the molecules and the statistical distribution of this internal energy. This mode of dealing with the effect of temperature and of catalysts will be given in Vol. III. The postponement is necessary because the physical idea regarding the significance of internal energy of the molecules has been extended by the introduction of certain considerations relating to the cause of reactivity in general, reactivity being ascribed to the absorption of radiation in terms of Quanta.

INFLUENCE OF PRESSURE ON REACTION VELOCITY.

In gaseous systems, the effect of increased pressure, if it brings about a volume change, will evidently increase the concentration terms, and the reaction will thereby go more rapidly. This effect has been considered in dealing with equilibrium in gaseous systems. In liquid systems the case somewhat resembles that of temperature influence, in that we know the effect of pressure on the *equilibrium* constant, *viz.*—

$$\frac{\partial \log K}{\partial p} = \frac{-dv}{RT}$$

but this expression, again, only gives us the change in the ratios of two velocity constants at different pressures. The above expression will be taken up later from a thermodynamic standpoint. Owing to the great incompressibility of liquids, this effect must be exceedingly small, and practically no work has been done upon the subject.

CATALYSIS IN HOMOGENEOUS SYSTEMS.

Positive Catalysis of Reactions.—First of all let us consider gaseous systems. It has been known for a long time (Dixon, 1880) that reactions between two gases such as carbon monoxide and oxygen will not take place unless water vapour is present. The reaction may be written simply—

$$2CO + O_2 \rightarrow 2CO_2$$

but this, of course, does not bring the water into play at all. Dixon virtually restated a proposition which had been put forward in 1794 by Mrs. Fulhame, namely, that the reaction takes place in two stages.

(1) CO reacts with H_2O to give CO_2 and nascent H

$$2CO + 2H_2O \rightarrow 2CO_2 + 4H$$

and (2)

$$\underset{\text{nascent}}{4H} + O_2 \rightarrow 2H_2O.$$

The water, therefore, causes the formation of the intermediate substance, nascent hydrogen. Dixon showed the probability of such a cycle of changes by demonstrating that H_2 is liberated from a heated mixture of carbon monoxide and steam, and also that hydrogen combines with oxygen to reform steam. Dixon further showed that other gases, such as sulphuretted hydrogen, ethylene, ammonia, pentane, and hydrochloric acid, will cause CO and O_2 to unite; while sulphur dioxide, carbon bisulphide, cyanogen, carbon tetrachloride, have no catalytic effect. Hence Dixon came to the conclusion that not only steam but all substances which will form steam under the conditions of the experiment, will cause carbon monoxide and oxygen to unite. This work may be regarded as demonstrating the intermediate compound view of catalysis.

Whilst intermediate compound formation certainly exists, in general, it is evident at the same time that the formation of intermediate compounds tells us nothing regarding the origin of the increased reactivity which positive catalysis obviously entails. To thoroughly understand the mechanism of a given catalysed reaction we must know not only the actual material changes involved, but at the same time the concomitant energy exchanges. The general problem included in the latter will be taken up briefly in Vol. III.

We now pass on to consider some cases of catalysis in solutions.

The most active catalytic agents in solution are $H^{\cdot}$ and OH' ions. We have already met with the effects of these, *e.g.* the catalytic effects of $H^{\cdot}$ ions on the inversion of cane sugar, or on the rate of hydrolysis of esters (by acids) in which, for dilute solutions of the catalysing $H^{\cdot}$ ions, the velocity of the reaction is directly proportional to the $H^{\cdot}$ ion concentration. For more concentrated solutions, however, this is not strictly accurate. The catalytic effect has been ascribed to $H^{\cdot}$ ions, because the catalysis by different acids at equivalent concentration—provided that the concentration is not too great—is the same. Further, if the dissociation of the catalysing acid is thrown back, say by the addition of a soluble neutral salt of the acid, the catalytic effect is also proportionally decreased provided the acid is a weak one; if it is strong the catalytic effect actually increases. This will be discussed later. It will be remembered that Wij's method for obtaining the ionisation constant of water by the aqueous saponification of methyl acetate is based on the catalytic effect of the $H^{\cdot}$ ion and the direct stoicheiometric action of the OH', the OH' ion in this case being 1400 times more effective than $H^{\cdot}$ at the same concentration. Since catalysts, such as those mentioned above, take no permanent part in many of the reactions which they catalyse, they cannot affect the equilibrium point finally reached.[1] This must mean—since the equilibrium constant K is simply the ratio of the opposing velocities—*that a catalyst affects both the direct and reverse reaction velocities to the same fractional amount.* In fact, this was used as the criterion for the catalytic process. It has been shown, however, that in some cases, not only does the catalyst act as such, but it likewise disappears to a certain extent, owing to its having participated in the reaction in a "secondary" manner. Hence the most general criterion for a catalytic effect is that one (or more) of the substances does not react according to any simple stoicheiometric equation. In fact, when we cannot state definitely the exact function of one of the constituents which takes part in a reaction, we put it down to catalytic effects. In other words, catalysis is a term for unsolved mechanism. Of course, there is nothing specially occult or subtle about the mechanism of a solute catalyst, such as an ion or a molecule, as far as material changes are concerned. Ultimately, when our information is more complete, it will be possible to write down a series of stoicheiometric equations which will represent completely the purely chemical changes involved. Already this can be done to a certain extent in a few cases. (A much more doubtful point is the part played by the solvent. We shall consider the solvent as a catalyst later.)

As an example of the kind of intermediate compounds which are formed in a catalysed reaction we may take the case of the hydrolysis of an ester, ethyl acetate, and the esterification of the corresponding acid, acetic acid, in the presence of HCl as catalyst. Apart from the catalyst the reaction is simply—

$$CH_3COOC_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH.$$

Each of these opposed reactions is catalysed to the same fractional extent by HCl. We shall suppose that the concentration of the HCl is not large enough to bring into play those effects already observed by Lapworth and Jones in connection with the equilibrium constant of the above reaction.

According to Falk and Nelson (*Journ. Amer. Chem. Soc.*, **37**, 1732, 1915), the catalytic effect of the HCl is due to the following series of reversible reactions:—

1. $CH_3COOC_2H_5 + HCl \rightleftarrows CH_3COOC_2H_5,HCl$ (binary oxonium compound).
2. $CH_3COOC_2H_5,HCl + H_2O \rightleftarrows CH_3COOC_2H_5,HCl,H_2O$ (ternary oxonium compound containing two tetravalent oxygen atoms).
3. $CH_3COOC_2H_5,HCl,H_2O \rightleftarrows C_2H_5OH,HCl + CH_3COOH.$
4. $C_2H_5OH,HCl \rightleftarrows C_2H_5OH + HCl.$

The ternary oxonium compound is common to both the direct and reverse reactions, and, therefore, the effect of the HCl is the same in both directions. There is also no disappearance of the catalyst, HCl, as a whole (except as a result of entirely secondary changes, *e.g.* the formation of ethyl chloride). Falk and Nelson assume that it is the ethoxyl oxygen which is tetravalent in reaction (1). As a matter of fact there is no means of distinguishing this experimentally from the possible tetravalency of the keto-oxygen in the ester molecule. The cryoscopic measurements of Baume and Pamfil (*Comptes Rendus*, 1911 and onwards) as well as those of Kendall (*Journ. Amer. Chem. Soc.*, 1914 and onwards) have demonstrated the real existence of such binary and ternary compounds as are assumed in the above mechanism. Kendall has discovered the important general rule that stable addition compounds of the above type are only found when there is a marked chemical contrast (acidic and basic) between the two reacting components. Thus in the additive compounds formed between organic acids and phenols, the stability is very much greater when the organic acid is strong and the phenol weak—or *vice versâ*—than in the case in which both substances exhibit the same degree of acidity. A similar generalisation holds for the addition compounds between two acids, or between an acid and a ketone, or between an acid and an aldehyde. This conclusion is likewise borne out by the results obtained by Baume and Pamfil. Thus it is shown that a compound exists between methyl alcohol and HCl, *viz.* CH_3OH,HCl; also between propionic acid and HCl, *viz.* C_2H_5COOH,HCl. It has also been found that the latter binary compound can add on a molecule of methyl alcohol, *viz.* C_2H_5COOH,HCl,CH_3OH. It is an interesting fact that propionic acid and methyl alcohol do not themselves form a binary compound, at least in so far as freezing-point measurements are capable of giving us information.

---

[1] Koelichen, *Zeitsch. Physik. Chem.*, 33. 149, 1900.

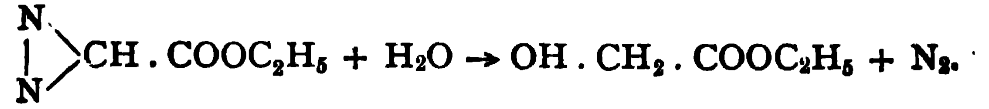
It follows from the above generalisation that HCl should be capable of giving a stable oxonium ternary compound, and therefore should exhibit marked catalytic properties. This is in agreement with experiment as will be more evident when we have discussed the "dual theory of catalysis". As a corollary we would expect acetic acid to exhibit weak catalytic properties as it should not form the necessary ternary compound to any appreciable extent. This is likewise in agreement with experiment. It should be noted particularly that *the above mechanism of the catalytic effect applies only to the undissociated molecule of* HCl. It tells us nothing about the known catalytic effect of the hydrogen ions, and in contrasting the behaviour of HCl and acetic acid in the above case, we have been thinking only of the relative catalytic influence of their respective undissociated molecules, and not at all of the $H^\bullet$ ion concentration which is determined by their respective degrees of ionisation. The probable function of the $H^\bullet$ ion is taken up in dealing with Goldschmidt's theory of ion-hydrates and ion-alcoholates (*vide infra*).

Ternary compounds, analogous to the above, are also probably formed in the case of $AlCl_3$ in the Friedel-Crafts' reaction, in the case of mercuric iodide, which acts as a positive catalyst for the union of alkyl sulphides and alkyl iodides (*cf.* Smiles, *Trans. Chem. Soc.*, **77**, 163, 1900), and also as a positive catalyst for the union of alkyl iodides and nitriles (*cf.* Hartley, *Trans. Chem. Soc.*, **109**, 1302, 1916).

In connection with the assumption made above that the undissociated molecule of HCl is a catalyst, mention may be made of the effect known as "neutral salt action". If we take a reaction which is catalysed by the $H^{\cdot}$ ions of an acid, and add, say, the sodium salt of the acid, then if the acid is a weak one, the catalytic effect will be decreased as already pointed out. But besides this effect, which is to be expected on the dissociation theory, we sometimes find an increase in the velocity—evidently due to specific catalysing properties possessed by the undissociated molecule of the acid. Thus Mellor, *Statics and Dynamics*, p. 280, quotes the case of cane sugar catalysed by 0·05N HNO_3, which gives the velocity constant 29·9; the addition of 0·4N KNO_3 raises the velocity to 33·9 instead of lowering it to 27·2. This point is considered later under the heading "Dual Catalysis". All ions (and molecules) have probably a catalytic effect, though $H^{\cdot}$ and OH' are quite unique in this respect. It is rather suggestive that the ions which form the solvent—for the great bulk of reactions have been studied in aqueous solution—are those which are most catalytically active. It is not improbable that the solvent itself plays a considerable part in every reaction in solution, and that the $H^{\cdot}$ and OH' ions assist this by continuously alternating ionisation and reformation of H_2O molecules.

Having discussed homogeneous catalysis in somewhat general terms, it is of interest to make ourselves acquainted with some of the more specific cases (*cf.* Bredig, "Altes und Neues von der Katalyse," *Biochem. Zeitsch.*, **6**, 283, 1907).

The first instance of measurements of catalysis by OH' ions by kinetic methods was the transformation of atropine into hyoscyamine, which occurs when a little alkali or other base is added to the system (W. Will and G. Bredig, *Ber.*, **21**, 2777, 1888). The same catalytic agent causes the partial transformation of glucose, mannose, and fructose into one another,[1] and the transformation of diacetone alcohol into acetone (Koelichen, *loc. cit.*). The catalytic action of $H^{\cdot}$ ion has been found to be present in a still larger number of cases. Mention has already been made of the sugar inversion and ester saponification. Besides these, the $H^{\cdot}$ ion acts catalytically in alcoholysis (in which an alcohol acts on an ester, thereby transferring an alkyl group thus: ethyl acetate + methyl alcohol → methyl acetate + ethyl alcohol (*cf.* Kolhatkar, *Trans. Chem. Soc.*, **107**, 931, 1915)), in the hydrolysis of lactones, and in the formation of anilides and esters (*cf.* H. Goldschmidt, to whose work we shall refer later), in the intramolecular change in diazo-amido compounds, and especially in the decomposition of diazoacetic ester, which has formed the subject of an extensive series of researches by Prof. Bredig and his pupils. Some of the numerical results obtained in the diazoacetic ester decomposition may be of interest. This ester is decomposed by water, as Curtius showed in 1883, according to the equation—



$$\begin{matrix} N \\ | \\ N \end{matrix}\!\!>CH.COOC_2H_5 + H_2O \rightarrow OH.CH_2.COOC_2H_5 + N_2.$$

---

[1] Lobry de Bruyn and von Ekenstein.

Fraenkel, under Bredig's direction (*Zeitsch. physik. Chem.*, 1907), showed that the rate of decomposition of the diazo ester in aqueous solution containing acid was proportional to the concentration of H˙ ions, as is shown by the following table:—

Catalysing Acid.	Concentration of Acid in gram-molecules per liter.	$C_{H^\cdot}$	Monomolecular Velocity constant k at 25° for diazo ester Decomposition.	Proportionality Factor between H˙ and k, *viz.* $F = \frac{k}{C_{H^\cdot}}$
Nitric . . .	0·00182	0·00182	0·0703	38·7
	0·000909	0·000909	0·0346	38·0
Picric . . .	0·000909	0·000909	0·0356	39·2
	0·000364	0·000364	0·0140	38·3
m. nitrobenzoic .	0·00990	0·00168	0·0632	37·7
Fumaric . . .	0·00364	0·00146	0·0571	39·1
Succinic . . .	0·00909	0·000724	0·0285	38·5
Acetic . . .	0·0182	0·000563	0·0218	38·7
			Mean =	38·5

The rate of the reaction was simply determined by reading at given times in a burette the amount of gas (N_2) given off from the solution, which was kept vigorously stirred to prevent supersaturation. The above data show that we are dealing with a simple H˙ ion catalysis. This is further shown by the effect produced by the addition of sodium acetate to the solution, which contained acetic acid as catalyst. Assuming the validity of the dissociation theory regarding "ionic product," one can calculate the quantity of H˙ ion in each case in presence of the sodium acetate. The following data were obtained:—

Concentration of Acetic Acid.	Concentration of Sodium Acetate.	$C_{H^\cdot}$ (calculated).	Velocity Constant k at 25°.	$F = \frac{k}{C_{H^\cdot}}$
0·0909	0	0·00127	0·0500	39·4
	0·00227	0·000584	0·0234	40·0
	0·00455	0·000351	0·0144	40·9
	0·00909	0·000192	0·0008	41·7
0·0182	0·000909	0·000276	0·0109	39·3

This diazo ester decomposition is a very delicate quantitative test for H˙ ion. Walker and his pupils have used it to determine the H˙ ion concentration in solutions of amphoteric electrolytes, such as glycocoll ($NH_2 . CH_2 . COOH$) which acts both as a base and as an acid in virtue of the simultaneous presence of NH_2 and COOH groups. The same method has also been employed by Bredig and Spitalsky (*Zeitsch. anorg. Chem.*, **54**, 265, 1907) to determine the extent of hydrolysis of potassium dichromate, which gives rise to chromic acid, which may be determined by the estimation of the $H^{\cdot}$ ion concentration.

Besides $H^{\cdot}$ ion and OH' ion catalysis other ions are effective, though in general to a less extent. Thus Bredig and Walton (*Zeitsch. physik. Chem.*, **47**, 185, 1904) have examined the catalytic effect of the iodine ion I', on the decomposition of H_2O_2 in aqueous solution. Equivalent solutions of sodium iodide, potassium iodide, and ammonium iodide were found to accelerate the reaction to the same extent, whereas cadmium iodide at the same equivalent concentration was much less effective, which is in agreement with the known fact that cadmium iodide forms complex ions in solution, as well as giving rise to I' ions. Some of the results obtained are as follows:—

Catalyst.	Concentration of Catalyst in Equivalents per liter.	Velocity Constant k_{25} (monomolecular).	$F = \frac{k_{25}}{C_{\text{catalyst}}}$
KI . . .	0·00699	0·00945	1·35
	0·03684	0·04761	1·29
NaI . . .	0·00616	0·00813	1·31
	0·03678	0·04810	1·32
NH_4I . . .	0·02656	0·0357	1·35
	0·03947	0·0529	1·34
$\frac{1}{2}CdI_2$ . . .	0·00976	0·00947	0·97
	0·0842	0·0453	0·54

The catalytic effect can be stopped by adding iodine (I_2), which converts I' ion into inactive I'_3, or by adding mercuric iodide, which forms a complex anion. The mechanism of the reaction, from the standpoint of the intermediate compound theory of catalysis, is represented thus—

Slow reaction (1) $H_2O_2 + I' \rightarrow H_2O + IO'$ (anion of hypoiodous acid)
Fast reaction (2) $H_2O_2 + IO' \rightarrow I' + O_2 + H_2O$
or summing both $2H_2O_2 \rightarrow 2H_2O + O_2$

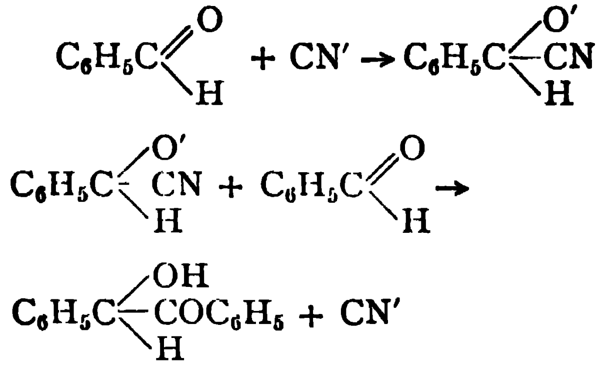
The dichromate ion Cr_2O_7'' was also shown to have a similar effect on the same reaction.

Somewhat analogous effects brought about by iodine have been observed by Hibbert (*Journ. Amer. Chem. Soc.*, **37**, 1748, 1915) in connection with the use of iodine as a "dehydrating and condensing agent". Very small quantities of iodine are required, and the action appears to be in all cases dependent on the formation of iodide and hypoiodite which react to regenerate the iodine I_2.

Bredig and Stern (*Zeitsch. physik. Chem.*, **50**, 513, 1905) also investigated the catalytically active CN' ion in the well-known reaction—

$$\underset{\text{Benzaldehyde.}}{2C_6H_5CHO} \rightarrow \underset{\text{Benzoin.}}{C_6H_5 . CO . CH(OH)C_6H_5}$$

which takes place in the presence of potassium cyanide, sodium cyanide or barium cyanide. The reaction is a bimolecular one, and the velocity constant depends on the quantity of CN′ ion present. The mechanism of the reaction is represented by—



(1) Very rapid $C_6H_5C\begin{smallmatrix}O\\ \\H\end{smallmatrix} + CN' \rightarrow C_6H_5C\begin{smallmatrix}O'\\CN\\H\end{smallmatrix}$

(2) Slow reaction $C_6H_5C\begin{smallmatrix}O'\\CN\\H\end{smallmatrix} + C_6H_5C\begin{smallmatrix}O\\ \\H\end{smallmatrix} \rightarrow$

$$C_6H_5C\begin{smallmatrix}OH\\COC_6H_5\\H\end{smallmatrix} + CN'$$

Benzoin.

In support of this it has been shown that the conductivity of potassium cyanide solution is diminished by the addition of benzaldehyde, thereby pointing to the formation of a compound.

Another well-known instance of catalysis is the effect of a small quantity of ferrous sulphate or molybdic acid on the reaction—

$$H_2O_2 + 2HI \rightarrow 2H_2O + I_2$$

One-millionth of a mole of molybdic acid per liter doubles the velocity constant of the reaction.

Autocatalysis.—Mention has already been made of H. Goldschmidt's work on ester formation and the catalytic effect of H˙ ions. That the effect is really due to these ions is shown by the following results (*Ber.*, **29**, 2208, 1896). Phenyl acetic acid was dissolved in ethyl alcohol, the solution being (0·2372) N. The reaction is—

$$C_6H_5 . CH_2 . COOH + C_2H_5OH \rightarrow C_6H_5CH_2 . COOC_2H_5 + H_2O$$

Since the alcohol is in large excess the reaction should be monomolecular. To obtain measurable velocities, picric acid was added, the particular concentration of this acid in Experiment I. being 0·01 N. Temperature 35° C. In Experiment II., a salt of picric acid, namely, *p*.-toluidine picrate (0·01 N) is added so that the dissociation of the picric acid may be thrown back, and if the catalytic effect is due to the H˙ ions, the velocity constant for the phenyl-acetic esterification should be decreased. In Experiment III. the same substances are present as in II., the *p*.-toluidine picrate being, however, 0·02 N.

$$\text{I. } k = 0{\cdot}0187;\ \text{II. } k = 0{\cdot}0086;\ \text{III. } k = 0{\cdot}0072$$

(The values for the constant in each case fall as time goes on, especially in I.)

Having established by the above and many other measurements, that H˙ ion does accelerate the rate of ester formation, it is evident that this effect must come in even when we add no catalysing acid, the effect being due simply to the hydrogen ions of the acid itself which is being gradually esterified. This is called autocatalysis. For a monomolecular reaction, catalysed by an ion, and proportionately to the concentration of the ion, we have—

$$\frac{dx}{dt} = k(a - x)C_{\text{ion}}$$

$(a - x)$ is *total acid* (dissociated and undissociated) present at any moment.

When the catalysing ion, *i.e.* the $H^{\cdot}$ ion, is produced from the acid which is being esterified (no other catalyst being added) the concentration of the $H^{\cdot}$ ion is a function of the time, being at any moment identical with the amount of dissociated unesterified acid, *viz.* $(a - x)m$, where m is the degree of dissociation of the acid. Hence in such a reaction we have—

$$\frac{dx}{dt} = k_1(a - x)^2 m$$

which has the form of a bimolecular reaction. Supposing m remains constant throughout the range examined, *i.e.* if measurements are made while the absolute concentration of the acid is not altered much, we can integrate the expression putting—

$$k_1 m = k_{25^\circ}$$

whence $$k_{25^\circ} = \frac{1}{t} \cdot \frac{x}{a(a - x)}.$$

The approximate applicability of this expression is shown in the subjoined table, the values given by making use of the monomolecular expression being added for comparison—

t hours.	$a = 12{\cdot}06$ (c.c. of titrating alkali).		
	$a - x$.	$\frac{1}{t}\log\frac{a}{a-x}$.	$\frac{1}{t}\frac{x}{a(a-x)}$.
47·8	11·18	0·000685	0·00676
118	10·24	0·000601	0·00626
191	9·24	0·000605	0·00663
291	8·30	0·000557	0·00648
407·5	7·50	0·000506	0·00618
554	6·58	0·000475	0·00622
672	6·07	0·000444	0·00605

These results and others not quoted are very much in favour of the applicability of the bimolecular formula, though the fall in the value of the constant with time shows that some secondary influence[1] is at work. The assumption that m is constant can scarcely be accurate when the range is as wide as that given, *viz.* when total acid concentration falls from 12·06 to 6·07, though the fact that the reaction is taking place in alcohol solution means that the dissociation is small, and possibly not very variable even over this range. (For Donnan's criticism, *cf. Ber.*, **29**, 2422, 1896.)

---

[1] The influence referred to is probably due to the water formed in the reaction; *cf.* the section dealing with catalytic effects of the solvent.

On the assumption that m is practically constant (and therefore Ostwald's expression $K(1 - m) = m^2(a - x)$ is inapplicable) one sees that a bimolecular reaction will be given by any one of three processes.

(1) If the reaction takes place between the undissociated molecules only—

$$\frac{dx}{dt} = k(1 - m)(a - x)$$

it is necessary to assume autocatalysis to obtain the bimolecular reaction—

$$\frac{dx}{dt} = k(1 - m)m(a - x)^2.$$

(2) If total acid reacts and there is catalysis (m constant)—

$$\frac{dx}{dt} = k(a - x)^2 m$$

i.e. bimolecular (Goldschmidt's case).

(3) If the reaction takes place between the alcohol and the ions of the acid,

$$\frac{dx}{dt} = km^2(a - x)^2$$

which is bimolecular and does away with the possibility of autocatalysis, for autocatalytic effects would produce a trimolecular reaction. Hence to decide whether autocatalysis is present or not, it is necessary to know whether it is the ions of the acid, or the undissociated portion which reacts, and whether m is to be regarded as constant or not. Since we know that $H^{\bullet}$ ion added "artificially" catalyses the reaction, it seems very reasonable at least to believe that autocatalysis must be present in the above case.

NEUTRAL SALT ACTION. THE DUAL THEORY OF CATALYSIS.

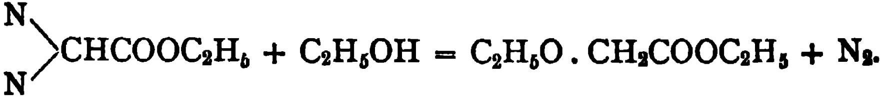
We have had occasion already to refer to neutral salt action, which has been[1] ascribed to the catalytic activity of the undissociated molecule of the acid to which the salt is added. The addition of sodium chloride, for example, to a solution of hydrochloric acid, throws back the dissociation of the acid, and consequently, if the catalytic activity of the undissociated molecule is greater than the catalytic activity of the $H^{\bullet}$ ion, the acid will, as a whole, exert a greater catalytic effect. If the catalytic activity of the molecule and the $H^{\bullet}$ ion happen to be identical, the addition of salt will have no accelerating effect. This, however, will be a rather exceptional case. If the catalytic activity of the undissociated molecule is feeble, less than that of the H$^{\cdot}$ ion, of course the addition of the sodium salt of the acid will diminish the total catalytic activity. The concept that undissociated molecules of acids as well as H$^{\cdot}$ ions possess in general catalytic properties is known as the Dual Theory of catalysis. The term was first suggested by Dawson (*Trans. Chem. Soc.*, **107**, 1426, 1915).

---

[1] It is necessary to point out, however, that recent work has tended to throw considerable doubt on the supposed activity of the undissociated molecule.

The theory itself appears to have been originated independently in 1907 by Senter (*Trans. Chem. Soc.*, **91**, 467, 1907) and by Acree (*Amer. Chem. Journ.*, **37**, 410; *ib.*, **38**, 258, 1907), and has been developed by these authors in later papers as well as by Arrhenius, Bredig and Snethlage, Goldschmidt, Lapworth, Taylor, Dawson, and others.

As an illustration of the necessity of introducing some such concept as the above, we may cite some of the results obtained by Snethlage (*Zeitsch. phys. Chem.*, **85**, 211, 1913). The reaction considered is the decomposition of diazo-acetic ester in absolute alcohol solution, *viz.*,



$$\overset{N}{\underset{N}{>}}CHCOOC_2H_5 + C_2H_5OH = C_2H_5O\,.\,CH_2COOC_2H_5 + N_2.$$

The catalyst is picric acid. The reaction proceeds as a monomolecular one, the values of the velocity constant quoted being those obtained by extrapolation to zero time, in order to avoid any influences due to subsidiary reactions. A number of salts of picric acid (toluidine picrate, tripropylamine picrate, etc.) were employed to throw back the dissociation of the acid. A few of the results obtained with additions of toluidine picrate are given in the following table:—

0·00909 N Picric Acid + *n* Toluidine Picrate.

Concentration of the Salt in Equivalents per Liter.	Ratio $\frac{\text{Concentration of Acid}}{\text{Concentration of Salt}}$.	Velocity Constant.
0	—	0·0580
0·000909	10·0	0·0485
0·001818	5·0	0·0410
0·004545	2·0	0·0300
0·00909	1·0	0·0220
0·02273	0·40	0·0180
0·0909	0·10	0·0145

On plotting these data and extrapolating through a short distance it is found that the curve cuts the vertical axis, the velocity constant axis, at a point well above zero. That is, on addition of a very large quantity of salt, the catalytic activity of the picric acid is positive and measurable. In presence of fairly large quantities of the salt the picric acid must be existing practically entirely in the undissociated state. Separate experiments showed that the salt itself, toluidine picrate, exerts an effect which is quite negligible. It is concluded therefore that the undissociated molecule of picric acid possesses catalytic properties, that is, the undissociated acid is a positive catalyst for the above reaction, although its effect is distinctly less than that of H· ion as is shown by the fall in the constant. Addition of tripropylamine picrate led to practically the same limiting value for the effect of the undissociated molecule of the picric acid.

Even in cases in which no salt is added, the concentration of the acid itself being varied, it has been found that the velocity constant in general does not remain strictly proportional to the H· ion concentration (as determined by conductivity experiments), but tends to increase somewhat faster than the H· ion concentration. If therefore we denote the catalytic effect of the undissociated molecule of the acid by k_m, and that of the H· ion by k_h, reckoning the gram-equivalent as the unit of mass, then, if γ be the degree of dissociation of a given catalysing acid, the total observed velocity constant k may be split up in the following way:—

$$k = k_h \,.\, \gamma \,.\, C + k_m \,.\, (1 - \gamma)C$$

where C is the total concentration of the acid in equivalents per liter.

Each acid may therefore be "characterised" by the numerical value of k_m/k_h. [We shall discuss this point later.] The ratio may be obtained by carrying out a number of measurements of velocity constants with different values of C and solving the resulting equations of the above type. Taylor (*Zeitsch. Elektrochem.*, **20**, 202, 1914) has collected a number of values of k_m/k_h for various acids which have been examined in connection with a number of different reactions. The following table will serve to give an idea of the order of magnitude of this ratio in a few cases:—

Reaction.	Solvent.	Catalyst Acid.	k_m/k_h.
Inversion of sucrose	Water	Hydrochloric	Ca. 2
Hydrolysis of esters	"	"	Ca. 2
Isomeric change of acetone	"	"	1·70
Hydrolysis of esters	"	Trichloroacetic	0·35
" "	"	Dichloroacetic	0·10
Isomeric change of acetone	"	"	0·50
" " "	"	Monochloroacetic	0·055
Inversion of sucrose	"	Formic	0·0067
" "	"	Acetic	0·0058
Diazoacetic ester reaction	Methyl alcohol	Picric	0·0162
Esterification of acetic acid	Methyl alcohol	"	0·0100
Diazoacetic ester reaction	Ethyl alcohol	"	0·1-0·06
Esterification of acetic acid	Ethyl alcohol	"	0·044

It is evident from these results that the strongest acids (hydrochloric, trichloroacetic) have the largest values for k_m/k_h, whilst the weak acids (acetic) have the smallest values. This distinction naturally suggests some connection with the so-called anomaly of strong electrolytes. Mention has already been made of Kendall's generalisation, *viz.* that addition compounds are most stable when there is a marked chemical contrast between the components. In general, therefore, the stronger the acid, the more stable are the binary and ternary compounds which the *undissociated molecule* of the acid is capable of forming (for example, with esters or sucrose). It may be concluded, therefore, that the catalytic effect of the undissociated molecule of an acid is due to the formation of such additive compounds, a view already expressed in connection with esterification and hydrolysis of esters. The strong catalytic power of undissociated HCl and the feeble catalytic power of undissociated acetic acid is thus partially explicable.

A further point is to be noted. If the catalytic effect of the undissociated molecule of the acid is due to the formation of addition compounds, it is obvious that the catalytic effect must vary to some extent with the nature of the reaction, for the stability of the various addition compounds will alter from case to case. This conclusion is borne out by the data quoted. Thus in the case of HCl we find a higher value for the ratio k_m/k_h in ester hydrolysis and sucrose inversion than we do in the isomeric change of acetone from the keto to the enol form. Whilst therefore the ratio k_m/k_h is characteristic of a given acid up to a point, it is to be remembered that the ratio alters with the nature of the reaction which is being catalysed by the acid. This is referred to in a slightly more detailed manner later.

The concept of dual catalysis has been investigated in a fairly comprehensive manner by Dawson and his co-workers in connection with the isomeric change of acetone (*Trans. Chem. Soc.*, **103**, 2135, 1913; *ib.*, **107**, 1426, 1915; *ib.*, **109**, 1272, 1916). The following table contains the values of k_m/k_h for a few *strong* acids in connection with this reaction. Two sets of values are given, according as we employ the conductivity expressions $\Lambda_v/\Lambda_\infty = \gamma$ (the degree of ionisation), or $\Lambda v\eta/\Lambda_\infty = \gamma$.

	$\gamma = \Lambda_v/\Lambda_\infty$.			$\gamma = \Lambda_v\eta/\Lambda_\infty$.		
Acid.	$k_h \times 10^6$.	$k_m \times 10^6$.	k_m/k_h.	$k_h \times 10^6$.	$k_m \times 10^6$.	k_m/k_h.
Hydrochloric . .	461	757	1·64	461	781	1·70
Hydrobromic . .	457	665	1·46	456	691	1·52
Trichloroacetic .	461	636	1·38	460	701	1·52
p-Toluene-sulphonic	472	593	1·25	—	—	—
Trichlorobutyric .	467	482	1·03	467	485	1·04

As we would expect, the values of k_h are practically constant, the catalysing agency being in all cases the $H^{\cdot}$ ion; on the other hand the values of k_m vary from acid to acid. It will be observed that in the case of the above acids the value of k_m/k_h is greater than unity; that is the catalytic activity of the undissociated molecule of these acids is greater than that of $H^{\cdot}$ ion. The value of the ratio for trichlorobutyric acid approximates most closely to unity; this is therefore an approximate illustration of the special case referred to previously in which the total catalytic activity is independent of the degree of ionisation of the acid and varies directly as the total concentration of the acid.

Dawson has likewise compared the values of k_m/k_h obtained in connection with the above reaction with the values found in connection with the hydrolysis of ethyl acetate and the inversion of sucrose (Taylor, *Meddel. K. Vetensk. Nobelinst.*, **2**, No. 37, 1913; Miss Ramstedt, *ib.*, **3**, No. 7, 1915; and Palmaer, *Zeitschr. phys. Chem.*, **22**, 492, 1897).

(All the values of k_m/k_h are based upon the simple formula $\gamma = \Lambda_v/\Lambda_\infty$ for the degree of ionisation.)

Catalyst.	Isomeric Change of Acetone.	Hydrolysis of Ethyl Acetate.	Inversion of Sucrose.
Hydrochloric acid . .	1·64	Ca. 2	1·48
Trichloroacetic . .	1·38	0·355	—
Trichlorobutyric . .	1·03	0·055	—
p-Toluene sulphonic .	1·25	—	—
Naphthalene-β-sulphonic	—	0·98	—

It will be observed that HCl shows the least marked variation in the ratio as the nature of the reaction alters. In general, however, the variation is very considerable.

Measurements of a somewhat similar character have been carried out by Acree (*cf. inter alia, Journ. Amer. Chem. Soc.*, **37**, 102, 1915; *ib.*, **39**, 376, 1917). In the first of these papers Acree has investigated the stoicheiometric activity of the ethylate ion and of the undissociated molecules of a number of alkali ethylates upon methyl iodide. Exactly the same principles hold good for these stoicheiometric reactions as for the so-called catalytic reactions. In the present case the reactions are—

$$C_2H_5O' + CH_3I \rightarrow C_2H_5OCH_3 + I'$$
$$C_2H_5ONa + CH_3I \rightarrow C_2H_5OCH_3 + NaI.$$

The following values for k_i, the activity term of the ethylate ion, and for k_m, the corresponding activity term of the undissociated molecule of the various alkali ethylates, were obtained at 25° C:—

Reaction.	k_i.	k_m.
Sodium ethylate and methyl iodide .	0·127	0·0594
(Repetition of above measurements).	0·1285	0·0581
Lithium ethylate and methyl iodide .	0·1367	0·0387
Potassium ethylate and methyl iodide	0·126	0·0687

It will be observed that k_i is approximately constant, as one would expect, for the process involved is the same in each case. On the other hand k_m varies with the nature of the alkali ethylate, being a specific quantity for each undissociated salt. It will also be observed that in the above reaction the activity of the ethylate ion is in all cases considerably greater than that of the undissociated alkali molecules, that is, the ion is mainly responsible for the production of the ether and alkali iodide. Analogous results were obtained in the case of the reaction of methylate and ethylate ions and the undissociated molecules of alkali methylates and ethylates with nitro and halogen substitution derivatives of benzene (*cf.* Acree, *Journ. Amer. Chem. Soc.*, **37**, 1909, 1915). Inthe case of the inversion of menthone, which has been investigated in a similar manner, the function of the ethylate ions and molecules is catalytic. Analogous results were obtained. The extensive investigations of Acree demonstrate very clearly that chemical reactivity, both stoicheiometric and catalytic,[1] must be attributed to undissociated molecules as well as to ions.

McBain and Coleman (*Trans. Chem. Soc.*, **105**, 1517, 1914) have investigated the problem as to whether the ratio k_m/k_h, in the case of catalysis by acids, varies with the temperature or not. The data used for calculation are those of Palmaer on the inversion of sucrose by HCl in aqueous solution. The conclusion arrived at is, that k_m/k_h diminishes as the temperature increases, the most probable values in the case of HCl as catalyst in presence of KCl in the above reaction being—

t° C.	k_m/k_h.
19-25	2·34
38-40	1·70
57	1·30

The decrease in activity of the undissociated molecule of the acid is due, certainly in part, to the fact that the addition compound, binary or ternary, tends to dissociate as the temperature rises. An exact relation would be obtained if a case were examined in which the equilibrium constant of the complex could be determined at various temperatures.

It is not easy at the present time to obtain a satisfactory value for the ratio k_m/k_h owing to the sensitivity of this ratio to the value chosen for the degree of ionisation γ. Thus, in the case of sulphuric acid, an examination of the available data leads to discordant results, some of them negative, according to the choice of γ. It is probable that in the case of H_2SO_4 the ratio is nearly unity, but it is impossible to state it more precisely.

In contradistinction to the Dual Theory of catalysis (in which a real catalytic activity is ascribed to the undissociated molecule as well as to the ion), the suggestion has been made that neutral salt action may be explained by an *increase* in the ionisation of the acid as a result of the addition of the salt, with a consequent increase in the H˙ ion concentration, which is regarded as *alone* possessing catalytic properties. McBain and Coleman (*loc. cit.*) review the available evidence and conclude that there is on the whole no experimental evidence for the supposed increase in ionisation. The Dual Theory represents, therefore, a very important contribution to the whole subject of chemical reactivity and catalysis.

---

[1] Ultimately the two terms are identical as far as material changes are involved.

CATALYTIC INFLUENCE OF THE MEDIUM ON CHEMICAL VELOCITY.

The relative influence of isolated solvents is shown by the following results taken from the work of Menschutkin (*Zeitsch. physik. Chem.*, **6**, 41, 1890) on the action of ethyl iodide on triethylamine—

$$C_2H_5I + (C_2H_5)_3N \rightarrow (C_2H_5)_4NI.$$

The reaction occurred as a simple bimolecular one, the velocity constant having the following values:—

Solvent.	Velocity Constant.	Dielectric Constant of Solvent.
Xylene . . .	0·00287	2·6
Benzene. . .	0·00584	2·6
Ethyl alcohol . .	0·0366	21·7
Methyl alcohol .	0·0516	32·5
Acetone . . .	0·0608	21·8
Benzyl alcohol .	0·1330	10·6

The velocity in benzyl alcohol is more than twenty times greater than in benzene, for example. It will be noted that the series of velocity constants follows approximately the series of dielectric constants for the solvents, but the rule is by no means general. It suggests that electrical effects are at the basis of the reaction, *cf.* the Nernst and Thomson rule. A striking contradiction of the rule is, that the velocity of the transformation of ammonium cyanate into urea is thirty times as fast in *ethyl alcohol* as in *water*, although the dielectric constant of water is four times as great as that of ethyl alcohol. The reaction velocity, therefore, is not to be referred to the physical properties of the solvent alone; the velocity is rather a specific chemical property of the reacting substances. An attempt has been made to find a connection between reaction velocity and the viscosity of the medium. That viscosity changes cannot account by any means for the whole effect is seen at once when one remembers the extraordinary large differences in reaction velocity occurring in solvents such as benzene and benzyl alcohol, where the viscosities are not very different. One may also draw attention to the work of L. Bruner and his pupils (*Bulletin de l'Academie des Sciences de Cracovie*) during the last few years on the effect of the solvent as determining the relative amounts of ring and side chain products formed, in the bromination of aromatic hydrocarbons. The conclusion arrived at is that an ionising solvent such as nitrobenzene assists the substitution in the ring, while a non-ionising (less-ionising) solvent such as carbon bisulphide and carbon tetrachloride has the effect of assisting side-chain substitution.

In spite of many years of research on the relation between the velocity of a reaction and the physical properties of the solvent no very satisfactory result has as yet been attained (*cf.* von Halban, *Zeitsch. phys. Chem.*, **67**, 129, 1909). One conclusion may be stated, however. The real distinction between a solvent catalyst and a solute catalyst, such as $H^{\cdot}$ ion, appears to be that the solute catalyst—if not present in too great concentration—hastens the direct and reverse reactions in such a way as to leave the equilibrium constant unchanged, whilst on the other hand, a solvent catalyst alters the equilibrium point.

The dual function of the solvent was first recognised and an attempt made to deal with it by van 't Hoff (van 't Hoff's *Lectures*, Vol. I., p. 221, English ed.). Van 't Hoff regards the total effect as (1) a true catalytic influence, involving equal acceleration of the direct and reverse reactions, and (2) a further influence, referred to above, which results in a change in the equilibrium point. Van 't Hoff attempted to get rid of this second effect by expressing the concentration terms of the reacting substances, not in gram-molecules per liter, but in terms of the solubilities of the reactants in different solvents. The resulting series of velocity constants—for the same reaction in a number of different solvents—may then be compared, and a measure of the relative *true* catalytic effects of the various solvents obtained.

By making use of van 't Hoff's expression, Dimroth (*Lieb. Ann.*, **335**, 1, 1904; *ib.*, **373**, 336, 1910; *ib.*, **377**, 128, 1910) showed in the case of the transformation of triazole bodies into anilides of diazoesters in a series of different solvents, that approximately the same velocity constant is obtained, indicating thereby that the various solvents in this reaction do not exert any true catalytic effect. Whilst this result was reached in connection with the decomposition of the triazole body, no quantitative relation could be obtained in the case of the reverse change. Van 't Hoff's method has, in fact, the serious limitation that it only seems to apply in practice to one direction in a reversible change, although its theoretical basis may easily be extended, as von Halban has pointed out, to the reverse reaction as well as to the direct. Von Halban has brought forward data which appear to stand in direct contradiction to van 't Hoff's conclusion. The fact is that van 't Hoff's idea has not been tested over as wide a range as it deserves to be.

Negative Catalysis in Homogeneous Systems.—By negative catalysis is meant the inhibiting action of certain substances on the velocity of a given reaction. Bigelow (*Zeitsch. physik. Chem.*, **26**, 493, 1898), for example, showed that in the oxidation of sodium sulphite by oxygen in aqueous solution, the rate was much reduced by the presence, in very small quantities, of substances, such as mannite, benzyl alcohol, aniline, and benzaldehyde. Analogous cases occur in which ions are the retarding agents.

As regards the kinetics of such reactions, Ostwald (*Allgemeine Chem.*, II., 2, 270) assumed that in the case of monomolecular reactions in which one of the products of the reaction had a retarding effect, *i.e.* we are dealing with *negative autocatalysis*, the expression for the velocity could be expressed as the difference of two terms, thus—

$$\frac{dx}{dt} = k_1(a - x) - x(a - x)$$

where x is the quantity of negative catalyst (or anticatalyst) produced at the time t. This expression has, however, been found not to hold good, and in Müller's experiments (*Zeitsch. physik. Chem.*, **41**, 483, 1902) on the hydrolytic decomposition of bromo-succinic acid, the assumption is made that the rate of reaction is directly proportional to the amount of bromo-succinic acid left, *viz.* $(a - x)$, and inversely as the amount of anticatalyst (HBr), or—

$$\frac{dx}{dt} = k\frac{a - x}{x}$$

which was found to be in agreement with the results.

The view put forward by Luther (*cf.* Titoff, *Zeitsch. phys. Chem.*, **45**, 662, 1903) as an explanation of negative catalysis is that it results from a partial destruction of some positive catalyst already present in the system. It is now fairly generally recognised that we can scarcely avoid the presence of catalysts of some kind, especially in the case of reactions which proceed in a liquid medium. In some cases repeated purification of the solvent has a marked effect upon the observed velocity constant.[1] Luther's explanation is applicable to Kulgren's results (*Zeitsch. phys. Chem.*, **37**, 612, 1901) obtained in the hydrolysis of ethyl acetate by caustic soda, in which addition of sucrose was observed to lower the rate of hydrolysis, this being due to a partial removal of caustic alkali as sodium saccharate. Similarly the inhibiting action of molecular iodine I_2, in the reaction between I′ ion and H_2O_2, which we have already mentioned, is due to the formation of the inactive I'_3 ion. Luther's explanation is certainly true in numerous cases, but it can scarcely be accepted at the present time as absolutely general.

Titoff (*loc. cit.*) has attempted to show that Luther's view of negative catalysis leads to the conclusion—which is in general agreement with experiment—that the observed velocity should be inversely proportional to the concentration of the negative catalyst. Titoff deals with the oxidation of sodium sulphite in solution by oxygen in presence of certain catalysts. As already mentioned Bigelow had investigated this reaction previously. Titoff finds that copper sulphate even in minute quantities is an excellent positive catalyst for the reaction. Titoff ascribes this to the copper ion. On the other hand, substances such as mannite or KCN are negative catalysts. Let us suppose that there is a small quantity of a positive catalyst A present in the solution, and that some negative catalyst B be added. The rate of reaction is thereby depressed. According to Titoff this is due to the removal of the free A substance by its union with B to form an inactive complex AB. The determining factor is expressed by the equilibrium—

---

[1] *Cf.* for example, W. Clayton (*Trans. Faraday Soc.*, 11, Part 2, 1915).

$$A + B \rightleftarrows AB$$

or

$$[A] = K\,.\,[AB]/[B].$$

The rate of reaction is proportional to [A] and therefore to K . [AB]/[B]. If the quantity of A is small compared with B, the value of AB will remain approximately constant, and we shall then have the rate of reaction inversely proportional to B. The limitations of this reasoning are obvious. It may be remarked, that since addition compounds of the type AB usually tend to dissociate as temperature rises, we would expect on the above mechanism that the negative catalyst should become progressively less efficient as a de-accelerator with rise of temperature. This point does not appear to have been examined in detail. To test Luther's view quantitatively it would be necessary to investigate a case in which the above equilibrium was directly measurable.

Bodenstein (Review of Chemical Kinetics and Catalysis, *Zeitsch. Elektrochemie*, **15**, 390, 1909) uses the inverse function as an explanation of the remarkable result obtained by Lapworth (*Trans. Chem. Soc.*, **93**, 2163, 2187, 1908) in the saponification of ethyl acetate by water in acetone solution, who found that the reaction, instead of being bimolecular as one would expect, was in reality independent of the water concentration, the expression—

$$\frac{dx}{dt} = kC_{\text{ester}} \text{ or } \frac{1}{t}\log\frac{a}{a-x} = k$$

being in satisfactory agreement with experiment. Water in organic solvents is known to have frequently an anticatalytic effect, and Bodenstein suggests the expression for the reaction velocity—

$$\frac{dx}{dt} = k\frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{water}}}$$

which evidently would explain Lapworth's result. Senter and Porter (*Trans. Chem. Soc.*, **99**, 1049, 1910) have put forward a similar view of negative autocatalysis, the anticatalyst being the hydrobromic acid formed in the hydrolytic decomposition of bromo-propionic acid in aqueous solution—

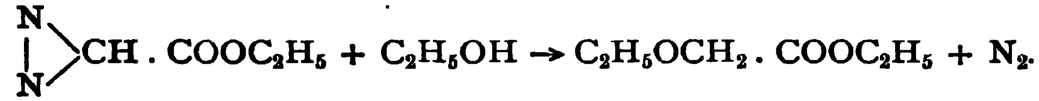
$$\text{CHMeBr . COOH} \xrightarrow{+H_2O} \text{MeCH}_2\text{OH . COOH} + \text{HBr}$$

and the analogous anticatalytic effect produced by nitric acid in the reaction between certain bromine substituted aliphatic acids, and silver nitrate in alcoholic solution, the velocity equation in the latter case taking the form—

$$\frac{dx}{dt} = \frac{k(a-x)^2}{x}.$$

(*Cf.* further, Senter, *Trans. Chem. Soc.*, **107**, 908, 1915.) Besides the cases of anticatalysis already mentioned, further attention must be paid to the anticatalytic effect of *water*, either when formed by the reaction itself or produced by actual addition to the system, the solvent in which the reaction occurs being one of the alcohols—usually ethyl alcohol.

Bredig's Investigations on Diazo Acetic Ester Decomposition in Alcoholic and Aqueous Alcoholic Solution.—Besides the decomposition of diazo acetic ester by water, its decomposition may also be effected by alcohol, and may take place in aqueous alcohol mixtures. In pure alcohol the reaction is—



$$\begin{matrix}N\\|\\N\end{matrix}\!\!>CH\,.\,COOC_2H_5 + C_2H_5OH \rightarrow C_2H_5OCH_2\,.\,COOC_2H_5 + N_2.$$

This reaction is likewise hastened by acids. Employing picric acid as catalyst of molar concentration 0·009N, Millar (*Dissertation*, Heidelberg, 1910; *cf.* also Millar, Braune, and Snethlage's papers in the *Zeitsch. physik. Chem.*, **85**, 129 *seq.*, 1913) found that in a pure alcoholic solution the velocity constant was 0·056. The dissociation of picric acid in ethyl alcohol is much less than in water. According to H. Goldschmidt,[1] it gives a dissociation constant in the former solvent, *viz.* $k_{\text{Ostwald}} = 0{\cdot}00058$, while it is known to be so strong an acid in aqueous solution that it gives none. Employing this value for the dissociation constant of the acid, it is found that a 0·009 molar solution is dissociated to the extent of 22·3 per cent., *i.e.* $C_{H^\cdot} = 0{\cdot}00203$, and hence the proportionality factor—

$$F' = \frac{k_{25}}{C_{H^\cdot}} = \frac{0{\cdot}056}{0{\cdot}00203} = 28.$$

This naturally differs from the factor F in aqueous solution as the reaction is of a different nature, *i.e.* in alcohol it gives rise to the substance—

$$C_2H_5O\,.\,CH_2\,.\,COOC_2H_5, \text{ instead of } OHCH_2\,.\,COOC_2H_5.$$

Starting with pure alcohol as solvent, and successively adding greater quantities of water, one would expect—since the dissociation of the catalyst (as far as increased conductivity results go) apparently steadily increases and also since the proportionality factor F, which one would think would come more and more into play, is greater than F′—that the velocity of decomposition of the ester should increase with increasing water addition (or decrease with increasing alcohol addition, supposing we started from the 100 per cent. water side). This latter case was realised by Fraenkel, as the following data show:—

---

[1] *Ber.*, 39, 111, 1906.

Concentration of picric acid = 0·000909 mol per liter.

Grams Alcohol in 100 grams of Reaction Mixture.	Velocity Constant k_{25}.
0	0·0356
3·31	0·0320 (mean)
6·69	0·0288 – 0·0290
14·2	0·0202 – 0·0206
21·9	0·0133 – 0·0134

Starting from the pure alcohol side, however, Millar found that the addition of water caused a decrease in the velocity of decomposition, followed later by an increase, *viz.*—

Concentration of picric acid = 0·009 mol per liter.

Mols H_2O per liter .	0	0·02	0·04	0·08	0·16	0·32	0·64
Velocity $k_{25} \times 10^3$.	57	53	47	42	33	26	18
Mols H_2O per liter .	1·28	2·56	5·12	10·24	15·36		
Velocity $k_{25} \times 10^3$.	11	6·4	4·4	4·9	7·0		

The values of k_{25} pass through a minimum in the region of 6 mols of H_2O per liter = 11 per cent. water.

This unexpected and complicated behaviour has not yet received satisfactory theoretical treatment. It is considered by Bredig and his pupils as analogous to results obtained by H. Goldschmidt in the case of ester formation, in which the water formed in the reaction had an inhibitive effect. It is doubtful, however, if Goldschmidt's theory will apply to the diazo-ester case. (The whole problem of the diazo-ester decomposition should be studied carefully by all interested in homogeneous catalysis. Besides the references given, *cf.* Bredig, *Verhandlung des Naturhistorisch-medizinischen Vereins zu Heidelberg*, N.F., **9**, 1907.)

In the above case of diazo acetic ester decomposition, the change in the nature of the *solvent* has had a most marked effect on the rate of the reaction. Other similar instances are known—for example, the decomposition of oxalic acid, which in concentrated sulphuric acid solution decomposes according to the equation—

$$(COOH)_2 = CO_2 + CO + H_2O.$$

Bredig and Lichty (*Zeitsch. Elektrochemie*, **12**, 459, 1906; *Journ. Phys. Chem.*, **11**, 225, 1907) showed that even the slightest trace of water had a marked inhibitive effect, indeed so marked that they put it forward as a method for determining traces of water in concentrated sulphuric acid. Thus, if 0·6 per cent. of water is present the reaction velocity constant is 0·018 at 70° C., while at the same temperature the presence of 3 per cent. water lowers the velocity constant to the value 0·00094; whether there is ionic catalysis here or not is unknown.

H. Goldschmidt's Theory of Esterification of Acids.[1]—The most striking point in connection with the formation of ester from an acid—such as phenylacetic, acetic, propionic, butyric, etc.—dissolved in alcohol, is that an addition of water, even though in small quantities, exerts a depressing effect upon the velocity constant, though to a much less degree than in the case of diazo acetic ester decomposition. This behaviour is of importance because water is one of the products of the reaction itself, a special case of negative autocatalysis. Goldschmidt has attempted to account for this behaviour in the following way.

As regards the formation of possible intermediate compounds, we might assume that in aqueous and alcoholic solutions of $H^\cdot$ ion, we have respectively ion-hydrates ($H_2O\,.\,H^\cdot$) and ion-alcoholates ($C_2H_5OH\,.\,H^\cdot$). Now when $H^\cdot$ (say from hydrochloric acid) is added for catalysing purposes to a pure ethyl alcoholic solution of acetic acid, we may suppose that in the first place a complex ion is formed, either between the acetic acid and the $H^\cdot$ ion, *i.e.* ($CH_3\,.\,COOH\,.\,H^\cdot$), or between the alcohol and the $H^\cdot$ ion ($C_2H_5\,.\,OH\,.\,H^\cdot$). The fact that the so-called hydrolytic constant *r*, to which we will refer in a moment, is practically independent of the nature of the acid undergoing esterification, is taken as evidence that the active catalytic agent is ($C_2H_5\,.\,OH\,.\,H^\cdot$) and that one can neglect ($CH_3\,.\,COOH\,.\,H^\cdot$) as probably not being formed at all. Further evidence that the active catalytic agent is ($C_2H_5OH\,.\,H^\cdot$), and not an addition product with the acid undergoing esterification, was given later by Goldschmidt (*Zeitsch. Elektrochemie*, **15**, 4, 1909). He showed that the *ratio* of the velocities of esterification of an organic acid, obtained when using hydrochloric acid and picric acid respectively as catalyst, was independent of the nature of the acid esterified.

Velocity Constant.	Acetic.	Propionic.	*n.*-Butyric.	Phenylacetic.
k in presence of $\frac{N}{10}$HCl	2·179	1·544	0·764	0·902
k in presence of $\frac{N}{10}$ picric acid	0·162	0·115	0·0582	0·655
Ratio $\frac{k_{HCl}}{k_{picric}}$	13·5	13·1	13·1	13·8

Similarly, using hydrochloric acid and sulpho-salicylic acid as catalysts, a constant ratio analogous to the above is obtained. The same alcohol, of course, is used throughout. Goldschmidt assumes, in fact, that the velocity of esterification is directly proportional to the concentration of the alcoholate ($C_2H_5OH\,.\,H^\cdot$). The *free* $H^\cdot$ ion is assumed ineffective. The mechanism of esterification is therefore—

$$(C_2H_5\,.\,OH\,.\,H^\cdot) + CH_3\,.\,COOH \rightarrow CH_3\,.\,COOC_2H_5 + H_2O + H^\cdot$$

The *total* $H^\cdot$ ion, *i.e.* the sum of the combined and free hydrogen ion, is therefore unchanged (theoretically).

---

[1] Goldschmidt and Udby (*Zeitsch. physik. Chem.*, 60, 728, 1907).

Now on the addition of water Goldschmidt assumes—and this is the kernel of his theory—that the following reaction occurs:—

$$\underset{\text{Ionalcoholate.}}{(C_2H_5OH\,.\,H^{\cdot})} + H_2O \rightleftarrows C_2H_5\,.\,OH + \underset{\text{Ionhydrate.}}{(H_2O\,.\,H^{\cdot})}$$

This reaction comes to an equilibrium point very rapidly. Evidently the complex ($H_2OH^{\cdot}$) has no esterifying power, in fact it is the complex which we would expect to saponify the ester, in ester saponification by catalytic $H^{\cdot}$ ion. Hence, if the above reaction takes place, the addition of water causes a decrease in the active esterifying agent ($C_2H_5\,.\,OH\,.\,H^{\cdot}$), and hence the addition of water causes, *ceteris paribus*, the velocity to decrease. This explains, therefore, the inhibitive or anti-catalytic effect of water. If we denote by—

ξ = the equilibrium concentration of the ionalcoholate ($C_2H_5\,.\,OH\,.\,H^{\cdot}$),
n = the concentration of the water added, *i.e.* the initial concentration,
x = the concentration of the water produced by the esterification, x also denotes the quantity of acetic acid which has disappeared,
r = the equilibrium constant of the ionhydrate, ionalcoholate equilibrium; r is called by Goldschmidt the hydrolytic constant,
η = equilibrium concentration of the ionhydrate ($H_2O\,.\,H^{\cdot}$), then, applying the law of mass action to the ion complexes equilibrium, we get—

$$C_{C_2H_5OHH^{\cdot}} \times C_{H_2O} = rC_{(H_2O\,.\,H^{\cdot})}.$$

The constant r contains the value of $C_{C_2H_5\,.\,OH}$, the solvent, which may be regarded as constant for small additions of water, this being the limits of applicability of Goldschmidt's considerations. Hence in symbols—

$$\xi \times (n + x - \eta) = r\eta$$

or

$$\eta = \frac{n + x}{r + \xi}\xi \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now consider the state of things before any water is added to the system at all. The concentration of the ionalcoholate ($C_2H_5OH\,.\,H^{\cdot}$) is ξ_0. When water is added, and this complex is reduced to ξ, the concentration term η evidently represents the quantity of ($C_2H_5\,.\,OH\,.\,H^{\cdot}$), which has disappeared in order to allow the formation of $H_2O\,.\,H^{\cdot}$. That is—

$$\xi_0 - \xi = \eta \quad . \quad . \quad . \quad . \quad . \quad (2)$$

But if at the stage before water is added b denotes the concentration of the solvent, *viz.* alcohol (about 17 gram-mols per liter at 25° C.), and c the total concentration of $H^{\cdot}$ of the catalysing acid,[1] we have for the reaction in which the active complex ($C_2H_5OH\,.\,H^{\cdot}$) is produced, *viz.*

$$H^{\cdot} + C_2H_5OH \rightleftarrows (C_2H_5\,.\,OH\,.\,H^{\cdot})$$

---

[1] Goldschmidt denotes the total acid by C, in his paper with Udby, *Zeitsch. physik. Chem.*, 60, 728, 1907. We may assume proportionality between the two.

the mass law relation—

$$\phi . c . b = \xi_0$$

where ϕ is the equilibrium constant.

Substituting this value of ξ in (2) we get—

$$\xi = \phi . b . c - \eta$$

or

$$\eta = \phi . b . c - \xi$$

and putting this value of η in (1) we obtain—

$$\xi = \phi bc - \xi\frac{n + x}{r + \xi}$$

or

$$\xi = \tfrac{1}{2}[\sqrt{(4\phi bcr) + (r + n + x - \phi bc)^2} - (r + n + x - \phi bc)] \qquad (4)$$

Now at any stage of the reaction, *e.g.* when water is present, the rate of esterification is proportional to the concentration of the acid, *i.e.* acetic acid, *viz.* $(a - x)$, and also proportional to the concentration of the catalyst ξ. That is—

$$\frac{dx}{dt} = k(a - x)\xi.$$

On substituting the value of ξ given by (4), and integrating, we obtain—

$$\frac{1}{2}kt = \frac{l + m}{q^2} \log \frac{Z_0 + m - l}{Z + m - l} - \frac{l - m}{q^2} \log \frac{Z_0 + m + l}{Z + m + l}$$

$$- \frac{2m}{q^2} \log \frac{Z_0}{Z} - \left(\frac{1}{Z} - \frac{1}{Z_0}\right) \quad . \quad . \quad . \quad (5)$$

where—

$$q^2 = 4\phi bcr$$
$$m = a + r + n - \phi bc$$
$$l = \sqrt{(a + r + n - \phi bc)^2 + 4\phi bcr}$$
$$Z_0 = \sqrt{(r + n - \phi bc)^2 + 4\phi bcr} - (r + n - \phi bc)$$
$$Z = \sqrt{(x + r + n - \phi bc)^2 + 4\phi bcr} - (x + r + n - \phi bc).$$

A more simplified treatment of the problem is obtained if we neglect η (the concentration of $(H_2OH^{\cdot})$) compared with $n + x$, the actual quantity of water present. Thus equation (1) becomes—

$$\xi(n + x) = r\eta, \text{ or } \eta = \frac{\xi(n + x)}{r}$$

and since as before—

$$\eta = \phi bc - \xi$$

we obtain by combining these two expressions—

$$\xi = \frac{\phi b . c . r}{n + x + r}$$

and substituting this in the expression—

$$\frac{dx}{dt} = k(a - x)\xi$$

on integration we obtain—

$$kct = (n + r + a) \log \frac{a}{a - x} - x \quad . \quad . \quad (5\text{A})$$

This latter equation applies fairly well when c and n are not too large. Goldschmidt used this form to determine r. Taking any two experiments with the same acid, and determining values of x, *viz.* x_1 and x_2 at times t_1 and t_2, we obtain from (5A)—

$$t_2\left[(r + n + a) \log \frac{a}{a - x_1} - x_1\right] = t_1\left[(r + n + a) \log \frac{a}{a - x_2} - x_2\right]$$

which allows us to calculate r. For the esterification of phenyl acetic acid, $r = 0{\cdot}151$; for acetic acid, $r = 0{\cdot}154$; for propionic acid, $r = 0{\cdot}146$; for monochloracetic acid, $r = 0{\cdot}142$. The mean value of r, Goldschmidt takes to be, $r = 0{\cdot}15$, and since this value varies so little from acid to acid, he considers that the active complex formed by the $H^{\cdot}$ ion of the catalyst, must be formed by the union of the $H^{\cdot}$ ion with the alcohol, *i.e.* the active complex must be $(C_2H_5OH \,.\, H^{\cdot})$, as we have assumed throughout. Although this conclusion is reasonable, it is still open to question. As regards some numerical values, the following may be quoted for the esterification velocity of phenyl acetic acid, hydrochloric acid being the catalyst; t has the usual significance, and k_0 denotes the "constant," calculated as a simple monomolecular reaction, assuming the catalyst has constant activity independent of the water present, *i.e.* no allowance being made for anticatalysis. It will be observed that k_0 varies very much with the time; kc denotes the constant calculated from the simplified equation (5A). The constant is fairly good. K denotes the value obtained from the complicated equation (5). The constancy of this value is better than any of the other values, though even this value is not very good, when the water value n is in any way considerable. This is probably due to the fact that while Goldschmidt assumes the complex $(H_2OH^{\cdot})$ to be quite inactive, its *saponifying* action is not negligible at the water concentration, $n = 0{\cdot}8$ mol per liter.

ESTERIFICATION OF PHENYL-ACETIC ACID.

$a = 0{\cdot}1$.	$c = 0{\cdot}1$.	$n = 0$.	
t hours.	k_0.	kc.	K.
0·104	0·854	0·314	52·2
0·304	0·803	0·322	52·4
0·504	0·758	0·320	50·9
0·903	0·707	0·322	52·0

ESTERIFICATION OF PHENYL-ACETIC ACID (*continued*).

a = 0·1.	c = 0·1.	n = 0·1.	
t hours.	k_0.	kc.	K.
0·1	0·555	0·328	51·3
0·3	0·537	0·330	51·6
0·604	0·520	0·336	52·2
1·1	0·496	0·334	52·3

a = 0·1.	c = 0·1.	n = 0·8.	
t hours.	k_0.	kc.	K.
0·307	0·149	0·327	48·5
1·5	0·125	0·278	47·2
3·0	0·116	0·267	39·6
6·0	0·111	0·265	38·7

a = 0·1.	c = 0·2.	n = 0·8.	
t hours.	k_0.	kc.	K.
0·25	0·282	0·622	47·7
0·60	0·279	0·621	47·4
1·25	0·274	0·616	46·9
2·50	0·262	0·603	46·4

Note that the constants decrease slightly with the addition of water, but the experimental error has a very large effect. See also Goldschmidt (*Zeitsch. physik. Chem.*, **70**, 627, 1910), also *Zeitsch. Elektrochemie*, **15**, 1909 (several papers).

It may be pointed out that the Goldschmidt theory will not account for the anticatalytic effect of water on the diazo acetic ester decomposition in the presence of $H^{\cdot}$ ion in alcoholic solution, for the anticatalytic effect in Goldschmidt's case depends on the fact that the complex $H_2O \cdot H^{\cdot}$ can have no esterifying power, or has indeed probably a saponifying influence. On the other hand, the complex $H_2O \cdot H^{\cdot}$ appears to be even more active as a decomposer of diazo acetic ester than the complex $(C_2H_5 \cdot OH \cdot H^{\cdot})$, *i.e.* $F > F'$, and hence any formation of $(H_2O \cdot H^{\cdot})$ at the expense of $(C_2H_5OH \cdot H^{\cdot})$ will cause an *increase* in the rate of the diazo acetic ester decomposition.

THE DISPLACEMENT EFFECT.

The writer suggests the above term to cover the effects introduced as a result of gradually displacing one reactant (generally a liquid), by another reactant (which may be a liquid or a dissolved solid), in a bimolecular reaction occurring in the liquid state. The effects referred to, which manifest themselves by an alteration in the value of the velocity constants of the reaction as the *initial* composition of the liquid system is altered, are not explicable on the basis of the law of mass action alone. They are evidence, in fact, of catalytic influences, introduced by at least one of the components, which is itself taking a definite stoicheiometric part in the reaction. The displacement effect has hitherto been examined, almost exclusively, in aqueous solutions, the water itself being the reactant displaced by addition of another reactant. In such cases water acts, in general, as a negative catalyst, *i.e.* its partial *removal*, by being replaced by, say, sucrose or methyl acetate, causing the velocity constant to rise in value. The phenomenon is scarcely likely to be a characteristic of water alone, although manifested in a particularly marked manner by this substance. It is rather to be regarded as a general effect, which is to be anticipated to a greater or less extent in all cases in which the nature of the medium as a whole is altered by the act of displacement. Hitherto, the phenomenon has not been the subject of very intensive examination. It is of importance, however, to indicate at least qualitatively its nature and magnitude.

As an actual case, let us consider the hydrolysis of methyl acetate in aqueous solution in presence of a known amount of H˙ ion. The reaction is—

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3OH + CH_3COOH.$$

The velocity constant k of this reaction, *viz.* $k = 1/t \log a/(a - x)$, where a stands for the final equilibrium value of the *decomposable* ester (a quantity somewhat less than the total ester added initially owing to a certain amount of reverse reaction), the constant k has been shown by Ostwald (*Journ. prakt. Chem.*, ii., **28**, 449, 1883) to vary with the initial concentration of the ester. Thus, at 25·2° C., with the catalyst HCl at a concentration of 2N/3, the following values of k were obtained in a series of experiments in which the ester concentration varied from 2 c.c. to 0·3 c.c. in a total reaction volume of 15 c.c. :—

With 2 c.c. of ester k = 24·19
„ 1 c.c. „ „ 21·96
„ 0·5 c.c. „ „ 20·71
„ 0·3 c.c. „ „ 19·91

That is, the greater the quantity of ester (or the smaller the quantity of water) in the system, the greater the velocity constant. Rosanoff (*Journ. Amer. Chem. Soc.*, **35**, 248, 1913) has pointed out that these velocity constants are not directly comparable because in each the concentration of the water is taken to be constant. During each individual run the water is indeed approximately constant, but as we pass from case to case the quantity of water necessarily alters. On allowing for the fact that the reaction is really a bimolecular one, and denoting the concentration of the water in each case by the general term w, the rate of reaction is given by—

$$dx/dt = k.w.(a - x).$$

On carrying out this "stoicheiometric" correction we obtain the following results in the above four cases :—

Ostwald's Monomolecular Constants.	k/w, *i.e.* the Constants Corrected for the Water Content.
24·19	1·888
21·96	1·590
20·71	1·447
19·91	1·378

The corrected constants are obtained by dividing those of Ostwald by the weight of water present in 15 c.c., the total volume of Ostwald's solutions. It will be observed that the divergence in the values of the constant is even greater than before. Rosanoff (*loc. cit.*) pointed out a similar divergence in the case of the inversion of sucrose, as more and more sucrose was added to the solution and water displaced thereby. The above correction, therefore, whilst justifiable and necessary, does not help us to explain the discrepancy. There is, however, a further possibility of a stoicheiometric nature which must be taken into account before we ascribe the phenomenon to catalysis. The reaction considered is reversible. Hence the strict velocity equation is—

$$dx/dt = k_1(b - x)\ (w - x) - k_2x^2$$

where k_1 is the true velocity constant of the direct reaction, k_2 that for reverse reaction, b is the initial concentration of methyl acetate in gram-molecules per liter, and x is the number of gram-molecules of either water or ester decomposed in time t. By integrating this expression values may be obtained for k_1 (*cf.* Lewis and Griffith, *Trans. Chem. Soc.*, **109**, 67, 1916). It was found that the values of k_1 did not differ much from those of k/w, namely the corrected Ostwald constants. The following table contains the values of k, k/w, and k_1, in the case in which 0·1 N HCl was used as catalyst at 25° C. The solutions throughout occupied 50 c.c. in volume.

Initial Concentration of Ester in Gram-molecules per Liter.	No. of c.c.'s of Ester in 50 c.c. of Solution.	Mean[1] Concentration of Water in Gram-molecules per Liter (w).	k.	k/w.	k_1.
1·156	5 approx.	49·69	0·000726	0·0000146	0·0000130
0·7013	3	51·86	0·000690	0·0000133	0·0000124
0·2425	1	54·25	0·000660	0·0000122	0·0000118
0·1305	0·5	54·86	0·000606	0·0000110	0·0000109

---

[1] The mean concentration of water is the concentration midway through an experiment, that is, when one half of the ester has been decomposed.

Similar variations in k were obtained with other concentrations of HCl, and also with trichloroacetic acid. It naturally suggests itself, in view of the known catalytic activity of undissociated HCl, that the change in k_1 may be due to a change in the degree of dissociation of the catalyst as the composition of the mixture varies from case to case. Experiments carried out to test this point showed that even when allowance is made for this effect the variation still persists. It appears, therefore, that the only possibility left is a catalytic one, in which the water acts as a *negative* catalyst relatively to the ester, as by removal or displacement of water the velocity constant is raised. Over the range of concentrations of ester cited above the velocity constant remained constant throughout any single run. When greater concentrations of ester are employed, the velocity constant k_1 altered during the course of a single experiment in the sense that its value rose as the reaction proceeded. This is evidently due to the removal of water in sensible quantities as a result of the reaction itself.

The mechanism of the negative catalytic effect of water in these cases has been suggested by Lewis and Griffith to be the following. In the first place it is assumed that the ester and water form an addition compound, which in the simplest case would contain one molecule of each, as a preliminary part of the hydrolysis proper. This addition would take place practically instantaneously, an equilibrium of the following kind being set up—

$$\text{ester} + \text{water} \rightleftarrows (\text{ester, water}).$$

Water itself is a strongly dissociating medium, and therefore when there is not much ester present this addition compound would be largely dissociated. As the water is displaced by addition of ester, the equilibrium *constant* itself will alter in the sense that the compound becomes more stable. That is, as water is displaced and the medium as a whole becomes less dissociating, the concentration of the addition compound will increase faster than it would if the equilibrium constant remained really constant. The rate of the observed reaction depends upon the concentration of the addition compound, and hence the rate is increased abnormally as water is removed. Since in the ordinary formulation of the process—from which k_1 is obtained—we do not take account of the addition compound at all, the abnormal rate of the reaction will manifest itself as an apparent increase in k_1. This accounts for the phenomenon qualitatively. If the equilibrium constant of the addition compound could be obtained as a function of the physical nature or percentage composition of the medium the idea suggested above could be tested quantitatively.

Since all liquids possess a certain degree of dissociating power, the phenomenon should be a general one, though less marked than in the case of water, which is characterised by an exceedingly great dissociating power. In the particular case in which the two reactants possessed equal dissociating properties it would be expected that the abnormality should be absent. It is a somewhat remarkable, though quite intelligible fact, that a substance such as water is required stoicheiometrically to permit the reaction to occur, but at the same time acts as a negative catalyst for the process. The view suggested above, that the negative catalytic effect of water is due to its high dissociating power furnishes also a qualitative explanation of the results obtained by Lapworth and Fitzgerald (*Trans. Chem. Soc.*, **93**, 2174, 1908) on esterification, although in this case the water does not play any stoicheiometric *rôle*.

CHAPTER X.

Systems not in equilibrium—Treatment from the kinetic standpoint—*Heterogeneous Systems:* Nernst's theory of heterogeneous reaction velocity—Heterogeneous catalysis—Langmuir's theory of surface action.

KINETICS IN HETEROGENEOUS SYSTEMS.

THE simplest conceivable type of heterogeneous reaction is the distillation of a pure liquid into a vacuum. If the vapour is withdrawn by some means, the rate of the production of the vapour by the liquid will be independent of time. It will likewise be independent of the mass of liquid present as long as any liquid remains. The reaction equation would be—

$$\frac{dx}{dt} = k, \text{ or } x_1 - x = kt.$$

A similar state of things exists in the formation of many radio-active products, such as niton from a radium salt. Further examples of heterogeneous velocities of a more complex nature are met with in the rate of dissolution of solids in liquids, *e.g.* benzoic acid in contact with water, or marble in contact with hydrochloric acid. In the process of dissolution of a solid, we know that at length a point is reached beyond which no more solid will dissolve, or rather at this concentration, which is simply the solubility of the solid, the rate of solution is just equal to the rate of precipitation, a heterogeneous equilibrium being established. The study of the phenomena involved in the dissolution of a solid in a liquid with, or without "chemical action," in the usual sense of the term, must be considered more closely. In the first place, it is evident that diffusion must play an important *rôle*. The fundamental expression for the diffusion of a substance already referred to in the preceding chapter was given by Fick (*Phil. Mag.*, [4], **10**, 30, 1855, being an excerpt from *Pogg. Ann.*, **94**, 59), in the form of a differential equation, based on Fourier's expression for heat conductance, *viz.*—

$$\frac{\partial y}{\partial t} = D\frac{\partial^2 y}{\partial l^2}$$

where y denotes concentration of the diffusing substance, t denotes time, and l denotes distance. D is the coefficient of diffusion, and may be defined as the quantity of substance, which during unit time will pass through unit sectional area from one stratum to the next adjacent one, the concentration gradient $\left(\frac{dy}{dl}\right)$ being unity.

The first investigation of importance on the subject of the velocity of dissolution of a solid in a liquid was undertaken by A. A. Noyes and

W. R. Whitney (*Zeitsch. physik. Chem.*, **23**, 689, 1897), who carried out measurements with benzoic acid and lead chloride, compressed into the form of small cylinders, which were rotated rapidly in water, the cylinder being removed from time to time, and the solute content in the aqueous solution determined analytically. The hypothesis which Noyes and Whitney formed, and which is fully borne out by their results, is that the solid substance is always surrounded by a very thin layer of saturated solution, and that the rate of dissolution is entirely dependent on the rate of diffusion of the solute from this saturated layer into the surrounding medium. This means that the *actual* dissolution of the solid is an extremely rapid process in comparison with the diffusion process, and it is the slower diffusion which determines the observed, *i.e.* the apparent, rate of dissolution of the solid. If S is the solubility of the solid, *i.e.* the concentration in the saturated layer, and x the concentration of the solute in the bulk of the solution at the time t, then the equation for the rate of dissolution is—

$$\frac{dx}{dt} = k(S - x)$$

assuming that the rate of diffusion, from one point to another, is proportional to the difference of the concentrations at these points. On integration this equation becomes—

$$\frac{1}{t}\log\frac{S}{S - x} = k$$

where k is the dissolution constant. It will be observed that this expression is similar in form to a monomolecular chemical reaction. This does not mean that the actual dissolution process proceeds according to the monomolecular law, but that the total apparent dissolution being determined by a diffusion process, one necessarily obtains an expression of the above type. As Nernst pointed out later (*Zeitsch. physik. Chem.*, **47**, 52, 1904), it is useless to attempt to settle the *order* of a heterogeneous reaction, such as that of marble dissolving in an acid solution, for the process which governs the reaction is the relatively slow diffusion, which will always cause the apparent dissolution velocity k to conform to a monomolecular type.

Some of Noyes and Whitney's results are as follows :—

Dissolution Velocity of Benzoic Acid into Water.

t (minutes).	x (average value).	k.
10	6·35	112·1
30	14·78 S = 27·92	109·1
60	21·60	107·5
10	8·74	163
30	18·49	157·1
60	24·79	160·1

Analogous results were obtained with lead chloride. It will be observed that for each series, with different specimens of solid, the values for k are reasonably constant, and hence the hypothesis with regard to the layer of saturation is confirmed. It will be noticed, however, that the absolute values in the different series are by no means the same. k must, therefore, be a composite quantity depending on the actual physical condition of the surface of separate portions of the solid, *i.e.* the surface area, and also, as was shown later, on the rate of rotation of the solid, because this affects the saturated layer.

The effect of the area exposed to the solution was more carefully investigated by L. Bruner and St. Tolloczko (*Zeitsch. physik. Chem.*, **35**, 283, 1900), who used very smooth surfaces, and measured the area before commencing, so that the dissolution velocity constant could be referred to unit area, *i.e.*—

$$\frac{dx}{dt} = kO(a - x)$$

and regarding O as constant throughout the expression, one obtains—

$$k = \frac{1}{Ot}\log\frac{S}{S - x}.$$

Experiments were carried out at a constant stirring rate with benzoic acid, phenyl-acetic acid, phenyl-propionic acid, acetanilide, and gypsum. The following data were obtained for benzoic acid in contact with water. Temperature 25° C., S equivalent to 12·86 c.c. of a given baryta solution, $O = 26{\cdot}8$ cm.^{2}

t (hours).	x.	k.
0·25	0·87	0·00454
0·50	1·60	0·00431
0·75	2·32	0·00431
1·0	2·91	0·00417
1·5	4·30	0·00439
2·0	5·30	0·00431
2·5	6·20	0·00427
3·0	7·25	0·00448
3·25	7·52	0·00438
5·5	10·23	0·00471
		Mean = 0·00439

The constancy is satisfactory. Bruner and Tolloczko also carried out measurements on benzoic acid and on gypsum at 35° C. For benzoic acid dissolution $k_{35^\circ} = 0{\cdot}0080$. Hence, for 10° rise the velocity has a temperature coefficient of 1·8 in the case of benzoic acid. In the case of gypsum $k_{25} = 0{\cdot}00233$, $k_{35} = 0{\cdot}00351$. Coefficient per 10° rise = 1·5. It will be observed that the coefficient for these heterogeneous reactions is smaller than the coefficient of a monomolecular reaction in a homogeneous system (usually 2 to 3 per 10° rise).

Bruner and Tolloczko noticed that in many of their experiments the surface of the solid was eroded. This would mean that the microscopic surface, as they call it, must be considerably greater at the end of the experiment than at the beginning. Yet a good constant has been obtained on the assumption that O remained constant. This can only be explained, as Bruner and Tolloczko point out, by assuming that there is a layer of saturated solution close to the solid, and the actual diffusion process really starts from the outer side of this layer, the "quadratic area of interface". Noyes and Whitney's assumption is therefore strongly supported by Bruner and Tolloczko's observations.

In the *Zeitsch. physik. Chem.*, **47**, 52, 1904, Nernst put forward a general theory of heterogeneous reaction velocity, which was experimentally confirmed by E. Brunner (*Zeitsch. physik. Chem.*, **47**, 56, 1904), and by the later work of others. According to this theory, the actual chemical reaction between, say, a solid such as marble and an aqueous solution of hydrochloric acid, is very rapid compared with the rate of diffusion of the hydrochloric acid, from the bulk of the solution into the Noyes-Whitney layer. According to Nernst, if O is the "effective surface area of the solid, *i.e.* outer area of the layer in contact with a solution whose volume is V, and δ the thickness of the layer, and if D is the diffusion coefficient of the diffusing substance, namely, hydrochloric acid, per unit area per second per unit concentration difference, then in time dt the quantity dx, or—

$$\frac{\mathrm{OD}(a - x)}{\mathrm{V}\delta}dt$$

of hydrochloric acid will diffuse into the layer. V comes into the expression in order to make $\frac{a - x}{\mathrm{V}}$ a concentration term, which denotes the actual concentration of hydrochloric acid in the bulk of the solution at the time t. But applying an equation of the Noyes-Whitney type to this process, we obtain—

$$dx = k(a - x)dt$$

and hence k, the dissolution velocity, may be expressed—

$$k = \frac{\mathrm{OD}}{\mathrm{V}\delta}.$$

The greater the surface area, the greater will k be, the faster the rotation of the solid, the smaller will δ become, and hence the greater will k be. For the rate of dissolution of benzoic acid in water, we can therefore write—

$$\frac{dx}{dt} = k(\mathrm{S} - x) = \frac{\mathrm{OD}}{\mathrm{V}\delta}(\mathrm{S} - x).$$

From the observed value of k, and the observed values of V, O, and D, we can calculate δ, the thickness of the layer, for a given rate of stirring.[1] Brunner calculated this as follows :—

---

[1] Brunner found that the dissolution rate (k) was $\propto$ ⅔ power of the rotation frequency.

Temperature = 20° C.

Reaction.	*k* (for stirring rate of 150 revolutions per minute).	D.	δ (for stirring rate of 150 per minute).
Benzoic acid (fused) in water	2·3	0·75	(20μ) = 0·020 mm.
Magnesia in benzoic acid .	1·55	0·75	0·029 "
" in acetic acid. .	2·05	0·95	0·028 "
" in hydrochloric acid and magnesium chloride .	8·1	6·7	0·050 "
Marble in hydrochloric acid and magnesium chloride .	11·0	6·7	0·036 "
Magnesium in benzoic acid .	2·1	0·75	0·0215 "
Silver acetate in water . .	1·55	1·0 – 0·8	0·039 – 0·031 "
Electrolysis of benzoic acid .	1·45	0·75	0·031 "

The values of δ are of the same order throughout, thereby pointing to the physical nature of the velocity process. The above data on the rate of solution of magnesia in benzoic and acetic acids show further that it is not the strength of the acid (benzoic is stronger than acetic), but their diffusion rates which determine the reaction velocity; for acetic acid reacts more rapidly than benzoic acid owing to its greater diffusion.

In the illustrations which have been given the characteristic common to all is that the chemical reaction velocity is very great compared with the diffusion rate. An exception to this occurs in the hydrolysis of esters suspended in water (H. Goldschmidt, *Zeitsch. physik. Chem.*, **31**, 235, 1899). With regard to criticism of the diffusion theory of heterogeneous reaction velocities, one may perhaps mention that of Meyer Wildermann (*Zeitsch. physik. Chem.*, **66**, 445, 1909), which is, however, of doubtful value.

As already pointed out, if the heterogeneous velocity is really that of a diffusion process, one will always get a monomolecular constant independent of the actual order of the more rapid chemical reaction, which accompanies the diffusion process. By way of recapitulation, the following characteristics of heterogeneous reaction may be noted.

(1) The connection between the reaction constant and the diffusion constant is given by—

$$k = \frac{\mathrm{OD}}{\delta \mathrm{V}}$$

and this must be verified by the data.

(2) Whatever influences the viscosity of the solution must necessarily alter D, and hence alter *k*.

(3) The rate of rotation of the body (or of the liquid surrounding the given body) must likewise alter the velocity constant.

(4) The temperature coefficient of *k* must be of the order of 1·28 for 10° rise (Trautz and Wedekind have found cases of *homogeneous* reaction velocities with very small temperature coefficients).

["On the factors which determine crystal habit," see R. Marc and A. Ritzel, *Zeitsch. physik. Chem.*, **76**, 584, 1911, who deal with the problem from a thermodynamic standpoint.]

Certain Radioactive Changes.—Radioactive changes are practically always heterogeneous, in that the physical state of the resultant is usually different from that of the reactant, *i.e.* a gas gives rise to a solid, or a solid gives rise to another solid, with which it is presumably immiscible. They cannot be dealt with in terms of the diffusion law and have therefore been introduced as illustrative examples, into the section dealing with *homogeneous* reactions. The problem of the rate of absorption of α or β rays by different media is, however, evidently a diffusion process, and attention may be briefly drawn to one or two cases. The Noyes-Whitney expression as such has not been applied. Instead, the monomolecular reaction expression, which we have seen is identical in form with the diffusion expression, has been employed and has been found to correspond to these processes very closely. Thus, in the case of α rays from radium[1] or polonium, the active preparation was covered with successive layers of aluminium foil, the ionisation produced in the air chamber above the foil being determined in the usual way by the rate of leakage from a charged electroscope. By this means it was found that the ionisation depended on the thickness of the aluminium layer according to the usual exponential or "compound interest" law, *i.e.* if I is the intensity of ionisation (which, of course, is a direct measure of the number of α particles) when the aluminium foil thickness is r, and I_0 is the intensity when there is no aluminium foil, then the following expression holds—

$$I = I_0 e^{-kr}.$$

This may be written—

$$\frac{1}{r} \log \frac{I_0}{I} = k$$

which is the more usual chemical form. This law is true as long as the thickness of the aluminium does not exceed a certain value. When this value is exceeded the ionisation in the chamber above falls much more rapidly, this evidently being due to the fact that the α rays are no longer getting through this thickness of foil. This gives the "range" of the α particles in aluminium. In addition to liquids and gases, metals are known to absorb the α rays, and the extremely simple and general rule is that the absorption is directly proportional to the density of the absorbing medium, and does not depend on its chemical constitution. This holds even when we compare two substances so dissimilar as air and aluminium. What has been said of α particles holds equally well for β rays, though these rays are, of course, much more penetrating. The density law holds in all cases with the exception of lead and tin.

---

[1] Rutherford and Miss Brooks, *Phil. Mag.*, July, 1902.

HETEROGENEOUS CATALYSIS.

It has long been known that a reaction which goes on extremely slowly by itself may be greatly accelerated if a piece of platinum or other substance is introduced into the system. Two important instances of the technical application of such heterogeneous catalysts are the "contact process" of sulphuric acid manufacture, and the preparation of chlorine by the passage of hydrochloric acid and oxygen over pumice impregnated with a copper salt, *e.g.* cupric chloride in the "Deacon Process". To systematise our considerations we may divide heterogeneous catalysis into two groups—

(1) Catalysis of a gaseous reaction by the introduction of a solid.

(2) Catalysis of a reaction occurring in solution, by means of a solid or a colloidal substance.

1. *Heterogeneous Catalysis in Gaseous Systems.*—Our information on this subject we owe chiefly to Bodenstein and his co-workers (*Zeitsch. physik. Chem.*, 1903, 1904, 1905, 1907). The most important case is that already mentioned, *viz.* the contact process of sulphuric acid manufacture. In this, sulphur dioxide and oxygen are made to combine at a fairly high temperature, the catalyst being platinum, in the form of sponge, wire, etc. The stoicheiometric equation is—

$$2SO_2 + O_2 \rightarrow 2SO_3$$

i.e. if this were also the reaction velocity expression, one would get a *termolecular* constant. Bodenstein found that this was not the case (an illustration of its inapplicability will be given later). The expression which was found to be most applicable was a modified monomolecular one, that is a monomolecular expression upon which was superimposed a term for the quantity of sulphur trioxide formed, which was found to retard the progress of the reaction, so that Bodenstein's expression is similar in form to that of a negative catalysis, which we have already studied. The expression for the rate of the reaction is as follows:—

$$\frac{dx}{dt} = \frac{k(a - x)}{x^{\frac{1}{2}}}$$

where $(a - x)$ represents the amount of sulphur dioxide at a given moment, and x is the amount of sulphur trioxide at the same time. This expression is quite different from that which one would expect from a reaction in a homogeneous system, *i.e.* a reaction which could go on in the absence of a solid catalyst. The above expression on integration becomes—

$$k = \frac{1}{t}\left(a^{\frac{1}{2}} \log \frac{a^{\frac{1}{2}} + x^{\frac{1}{2}}}{a^{\frac{1}{2}} - x^{\frac{1}{2}}} - 2x^{\frac{1}{2}}\right).$$

(It becomes a little more complicated if one allows for the addition of some sulphur trioxide at the beginning: *cf. Zeitsch. physik. Chem.*, **60**, 13, 1907.)

The following data are taken from a typical experiment by Bodenstein :—

k is calculated as above. Temperature = 248° C.

"a" (SO_2) = 370·4 mm. mercury.

t (min.).	5.	10.	15.	20.	30.	40.	50.	60.	70.	80.	90.	100.	120.	150.
x . .	64·3	97·0	120·9	141·1	174·9	198·8	223·5	241·0	255·2	269·5	281·2	292·1	309·7	329·2
k . .	0·208	0·205	0·201	0·199	0·199	0·194	0·200	0·199	0·196	0·199	0·200	0·202	0·205	0·209

Mean *k* = 0·201.

In the above case the quantities of sulphur dioxide and oxygen were chosen initially equivalent. Bodenstein showed that on employing excess oxygen no effect was introduced—*k* was still constant throughout any series of determinations, and its value was very close to that obtained from the equivalent mixtures at the same temperature. With sulphur dioxide in excess, however, the constant was no longer good, and its absolute value was considerably lower than in the case in which the two gases are present in equivalent quantities. To account for this remarkable behaviour of a reaction which one would naturally have supposed to be termolecular, Bodenstein assumes that the velocity of combination of sulphur dioxide and oxygen at the surface of the platinum is extremely rapid, and that the velocity of the reaction actually measured is that of the diffusion of sulphur dioxide up to the surface of the platinum, this diffusion being hindered by the accumulating quantity of sulphur trioxide which is formed at the platinum surface, and through a layer of which the sulphur dioxide has to pass.[1] This assumption would lead us to expect an apparently monomolecular effect modified by a negative catalysis term involving the sulphur trioxide concentration. That the sulphur trioxide term appears as an exponential ($\frac{1}{2}$) will be rendered intelligible when we remember that the layer of sulphur trioxide must be of the nature of an adsorption layer, the surface concentration being generally (concentration in bulk)^n. Bodenstein applied his equation to the data of earlier experimenters, notably those of Bodländer and von Köppen, with the following results. k_3 is added for comparison, it denotes the "constant" of a *ter*molecular reaction. It will be observed that the values of *k* are extremely constant.

---

[1] Bodenstein's views must, however, be considered in the light of Langmuir's theory. See p. 461 *seq.*

t (hours).	$x(SO_3)$.	$k_3 \times 10^{10}$.	k (Bodenstein), Temp. = 182° C.
0·5	12	183	0·0043
1·0	20	161	0·0046
1·5	27	153	0·0049
2·0	32	140	0·0049
2·5	36	131	0·0047
3·0	40	117	0·0046
3·5	43·5	119	0·0046
4·0	46·5	115	0·0044
5·0	52	108	0·0043
6·0	57	103	0·0041
7·0	62	101	0·0041
8·0	67	101	0·0041
9·0	72	101	0·0041
10·0	76	100	0·0041
11·0	80	100	0·0041
12·0	84	100	0·0041

In Bodenstein's words (*l.c.*, p. 61) "a full explanation of all the phenomena (of heterogeneous catalysis of gas reactions) is given by the assumption that the reaction process is retarded by the product of the reaction in those cases in which this product is more easily condensable and more easily absorbed than the initial reactants themselves. There is in fact an adsorption layer, or in certain cases an ordinary liquid or solid skin formed upon the catalyst, through which the reactants must pass by diffusion in order to come into contact with the catalyst, where they react with practically instantaneous velocity."

For further details Bodenstein's papers must be consulted. A natural inference drawn by Bodenstein, from the results obtained in heterogeneous catalysis of gaseous reactions in general, is that the walls of the vessel which contains the gas mixture must also act in a similar manner, for Bodenstein's theory of catalysis is essentially a physical one, and catalytic properties ought to be possessed by every kind of surface. He showed this to be actually the case, thereby explaining certain anomalies which had been noted by previous experimenters. No gaseous reaction therefore is entirely uncatalysed, for the containing vessel must also exert an effect, though by suitable arrangement this may be made extremely small. Practically the first instance in which this phenomenon was carefully examined was when van 't Hoff (*Etudes*, 55, 1884) showed that the rate of polymerisation of cyanic acid depended upon the superficial area of the walls of the vessel. On heating the same quantity of cyanic acid in a simple bulb and in a spiral respectively, it was found that the rate of polymerisation was much greater in the latter case.

2. *Heterogeneous Catalysis in Liquid Systems.*—The catalytic agents in such cases are solids like platinum sponge, or colloidal particles such as are found in colloidal platinum solution, or enzymes, which very closely resemble colloidal particles. To show the similarity in action

between a colloidal solution of platinum and a blood enzyme (blood katalase), one may quote the respective data obtained by Bredig and Senter for the decomposition of hydrogen peroxide in aqueous solution by their means.

Blood Katalase (Senter).			Colloidal Platinum (Bredig and Müller von Berneck).		
t (mins.).	$C_{H_2O_2}$.	k (Monomolecular).	t.	$C_{H_2O_2}$.	k (Monomolecular).
0	39·7	—	0	47·4	—
5	32·2	0·0175	10	37·9	0·0097
10	26·7	0·0163	20	30·0	0·0099
20	17·8	0·0176	30	23·6	0·0101
30	11·6	0·0185	40	18·2	0·0104
50	4·8	0·0191	60	11·0	0·0106

Note that the reaction is monomolecular (or apparently monomolecular in both cases). Owing to the similarity in behaviour between colloidal metal solutions and enzymes, Bredig has called the former inorganic ferments (*cf.* Bredig's monograph, *Anorganische Fermente*). Bredig (with Teletow, *Zeit. Elektrochemie*, **12**, 581, 1906) has also shown in the case of the catalytic decomposition of hydrogen peroxide in aqueous solution by means of a cylinder of platinum foil rotated at a constant rate, that the reaction velocity constant is a monomolecular one, but that it differs from the ordinary monomolecular constant in homogeneous systems in that the numerical value of the constant is inversely as the volume of the solution. A few of Bredig's results are :—

Constant rotation frequency (245 revs. per minute).

Volume in c.c.	0·4343k at 25° C.
450	0·0060
675	0·0046
1350	0·0020

It is found in fact that kV is constant.

Bredig and Teletow also verified Bruner's conclusion as regards the "quadratic dimensions" of the foil being the effective surface, which we have already seen is due to the thin saturated layer being the actual surface of reaction. An excellent account of heterogeneous catalysis is given by Bredig in his *Vortrag* (already alluded to in the preceding chapter). For our present purpose a very useful summary of the theories of heterogeneous catalysis is given by Denham (*Heidelberg Dissertation*, 1909, *Zeitsch. physik. Chem.*, **72**, 641, 1910), which will be fairly closely followed here. First let us take some typical instances of heterogeneous catalysis. The effect of catalytic agents on the rate of dissolution of solids is very clearly shown by violet chromic chloride (insoluble), which only dissolves very slowly in water, but may be made to do so very quickly if a minute trace of chromous chloride is present. (It is assumed that the reaction here is—

$$CrCl_3 \text{ (insoluble)} + CrCl_2 = CrCl_2 + CrCl_3 \text{ (soluble)}$$

the newly formed chromous chloride again reacting with further quantity of insoluble chromic salt.)

The dissolution of impure zinc (*i.e.* containing traces of iron) in hydrochloric acid might also be looked upon as heterogeneous catalysis. The actual mechanism in this process is fairly well understood, *viz.* the production of short circuits between pieces of iron and zinc, and the consequent electrolysis and dissolution of zinc, which has a much greater solution pressure than the iron. The most frequently investigated case is the decomposition of hydrogen peroxide, which always takes place according to a unimolecular law. Hydrogen peroxide solutions can be decomposed with the evolution of oxygen, by colloidal platinum, and by spongy and solid platinum. Teletow (Bredig and Teletow, *Zeitsch. Elektrochemie*, **12**, 581, 1906) has shown also that in the latter case the decomposition of hydrogen peroxide follows the Nernst diffusion theory, first, in that it is apparently monomolecular, secondly, in that the rate decreases when the solvent is made more viscous by the addition of sugar to the water, and, thirdly, by the fact that the temperature coefficient is only 1·28 for 10° C. Platinised platinum has been found a very efficient catalyst for the oxidation or reduction of ions. Thus Oberer (*Diss.*, Zurich, 1903) observed an increase in the oxygen evolution from a solution of cobaltic sulphate (reduction taking place) on introducing a small piece of platinum wire, and Manchot and Herzog (*Ber. chem. Gesell.*, **33**, 1742, 1900) found that platinum exerted an accelerating influence on the (oxidation) reaction—

$$Co(CN)_6^{''''} + H^{\cdot} \rightarrow Co(CN)_6^{'''} + H$$

Spencer and Abegg (*Zeitsch. anorg. Chem.*, **44**, 379, 1905) also showed that thallous ions could be transformed into thallic ions, under similar conditions as regards catalyst (oxygen gas being present at the same time). Diethelm and Förster (*Zeitsch. physik. Chem.*, **62**, 129, 1908) have also investigated the reaction—

$$\underset{\text{Titano sulphate}}{Ti^{\cdot\cdot\cdot}} + H^{\cdot} \rightarrow \underset{\text{Titani sulphate}}{Ti^{\cdot\cdot\cdot\cdot}} + H$$

which takes place in acid solution [*i.e.* H˙ present] at a platinum cathode. The same reaction was comprehensively studied by Denham (*l.c.*), who employed a rapidly rotating platinum gauze cylinder as the catalyst, and who showed that the above reaction was strictly monomolecular (Denham, it may be remarked, used strongly acid solutions, H˙ being thus constant). Denham also succeeded in observing the equilibrium which is reached in the above reaction by approaching it from both sides (*i.e.* hydrogen gas is either absorbed or evolved according to circumstances). As regards the effect of temperature, Denham found a temperature coefficient of 1·29 for 10°, *i.e.* a very small one.[1] A heterogeneous catalyst hastens a reaction, and the greater the surface exposed, the greater is the reaction velocity. As a rule, however, the catalyst does not affect the equilibrium constant (when such is measurable). Such appears to be the case, as we find the catalyst at the end of the experiment in exactly the same amount, and in exactly the same chemical or physical state as at the commencement. Cases are known, however, to which the term "catalysis" is applied, in which the catalyst is itself altered. In such cases it has taken a permanent part in the reaction, and the equilibrium (if such is measurable) will have been correspondingly shifted.

Having given some typical instances of reactions catalysed heterogeneously, mention must be made of a characteristic peculiarity, namely, the poisoning of the catalyst. Many catalysts after some use lose their efficiency. This is particularly true of colloidal metal solutions and enzymes. Considering the familiar reaction, namely, the decomposition of aqueous solutions of hydrogen peroxide, it has been noticed that very small traces of hydrocyanic acid, iodine solution, mercuric chloride, destroy the activity of ferments, and Bredig found quite an analogous behaviour in the case of colloidal metals. Thus, in order to reduce the rate of decomposition of hydrogen peroxide, by a given solution of colloidal platinum[2] to *one-half* its normal value, it is necessary to have the following substances present at the concentrations:—

HCN	5×10^{-8} normal
ICN	7×10^{-8} "
I_2	7×10^{-6} "
$HgCl_2$	$2·5 \times 10^{-6}$ "

Senter also found that, using blood katalase as the catalyst for the same reaction, the normal value was reduced to ½ in presence of—

$$\frac{N}{1 \times 10^6}\ HCN\,; \text{ or } \frac{N}{5 \times 10^4}\ I_2\,; \text{ or } \frac{N}{1 \times 10^6}\ H_2S\,; \text{ or } \frac{N}{2 \times 10^6}\ HgCl_2.$$

The striking similarity between colloidal solutions and enzymes is here clearly brought out.

Pulsating Catalysis.—Examples of *periodic* velocities are to be found, for example, in the dissolution of chromium in acids, and in the electrolytic passivity of iron. Bredig discovered a much more reproducible instance, namely, the pulsating catalytic decomposition of hydrogen peroxide at a mercury surface. Slight additions of salts, alkalies, or acids had a marked effect. The source of this remarkable phenomenon was found to be an explosive unstable peroxide of mercury HgO_2, which has been isolated by von Antropoff (*Zeitsch. physik. Chem.*, **62**, 513, 1908).

---

[1] Other interesting results obtained by Denham, such as the quantitative reduction of hydrocyanic acid to methylamine by hydrogen gas in presence of platinum gauze, cannot be referred to here at length.

[2] Containing $\frac{1}{10^6}$ atoms of platinum per liter.

Theories of Heterogeneous Catalysis.—One may divide these theories into two classes, the chemical and the physical. The chemical view consists in supposing the existence of intermediate chemical compounds which are unstable; the physical view explains the phenomenon as due to the condensation or increase in concentration of the reactants at the surface of the catalyst—such increase in concentration being brought about by capillary forces.

As an example of the chemical view one may quote the following from Bredig's *Anorganische Fermente*: "Haber's view that platinum catalysis in the decomposition of hydrogen peroxide consists in an alternate oxidation and reduction of the metal according to the equations—

$$yH_2O_2 + nPt = Pt_nO_y + yH_2O$$
$$Pt_nO_y + yH_2O_2 = nPt + yH_2O + yO_2$$

seems to me to be the best explanation of the phenomena at present known".

The only outstanding instance in which the active intermediate compound has been isolated is the peroxide of mercury, HgO_2; there is no evidence for the existence of an intermediate compound in the catalysis of the same reaction by platinum, either as solid metal or in the colloidal state. In fact Wöhler (*Ber.*, **39**, 3538, 1906; **42**, 3326, 1909) actually showed that PtO and PtO_2 were less catalytically active than platinum itself in the "contact process" (sulphur dioxide + oxygen), but that, as the reaction was continued, the activity of the catalyst was increased, and analysis showed at the close of the reaction that the oxides had been completely reduced to metal. It is still more difficult to conceive that an oxide is the actually active catalyst in reactions where hydrogen gas is evolved, *i.e.*—

$$Cr^{\cdot\cdot} + H^{\cdot} \rightarrow Cr^{\cdot\cdot\cdot} + H$$
$$Ti^{\cdot\cdot\cdot} + H^{\cdot} \rightarrow Ti^{\cdot\cdot\cdot\cdot} + H$$

No proof, it may be mentioned, has been brought forward that a platinum hydrogen compound exists.

It is very significant that catalytic properties are usually possessed by those metals which can exist in a higher or lower state of oxidation, *i.e.* the polyvalent metals. Several illustrations of the catalytic effects of such metals and their oxides will be given in the section dealing with some technical applications of catalysis. The same idea has been applied in cases in which the system is considered to be homogeneous. Thus, in dealing with the drying of oils, *i.e.* the oxidation of oils, in presence of soluble metallic catalysts, or "driers," Mackey and Ingle (*Journ. Soc. Chem. Industry*, **36**, 317, 319, 1917) state that the more oxides a metal can form the greater the catalytic power. It looks as though we had to do with alternate oxidation and reduction of the metal, *i.e.* removal of an electron from the metal atom or ion, and its subsequent addition.

That there is some close connection between the variability in valency and the possession of catalytic properties is now very generally recognised, although the nature of the connection is quite obscure.

The physical theory of catalysis—which we have already mentioned in connection with Bodenstein's work—may be said to have been put forward for the first time by Faraday (1834), who considered that the reactants (gases) were bodily absorbed by the metal. J. J. Thomson put forward a modified form of this, in that it is supposed that capillarity is the origin of the effect, which thus becomes a surface phenomenon. This view has received more support than any other.

Gibb's fundamental expression for adsorption (see Vol. II., Chap. XI.) is—

$$\Gamma = \frac{-C}{RT} \cdot \frac{d\sigma}{dc}.$$

If δ is the thickness of the adsorbed layer, then the concentration in the layer is $\frac{\Gamma}{\delta}$, and this is the term for the active mass of the solute—supposing we are dealing with a liquid solution—at the surface of the catalyst. This concentration term is much greater than that in the bulk of the solution, and hence the reaction goes more quickly when the solid is present—the actual velocity, we assumed, being the rate of diffusion of the reactants through the resultants. Let us examine some of the characteristics of certain heterogeneously catalysed reactions and see how the adsorption theory fits the facts. Bredig and Muller von Berneck found that the catalytic decomposition of hydrogen peroxide by colloidal platinum was not strictly monomolecular, as the constant rose when the hydrogen peroxide concentration was small. Freundlich (*Kapillarchemie*, p. 382) ascribes this to adsorption. In adsorption, as the bulk concentration of the substance (H_2O_2) is increased, the concentration of the same substance at the colloid surface likewise increases, but *less* rapidly, and finally reaches an asymptotic stage, *i.e.* a stage at which the surface concentration is practically independent of the bulk concentration over a certain range. Over this range the reaction velocity will be constant, because the surface concentration is nearly constant, that is $dx/dt = k$ (*cf.* Armstrong's measurements with lactase quoted below). Let us now think of the above relations between surface and bulk concentrations in the reverse order, *i.e.* as reaction proceeds and the H_2O_2 is progressively used up. When this has gone on for a time the concentration of H_2O_2 in the surface layer will become *proportionately* greater (*i.e.* with respect to the bulk concentration) than it was at an earlier stage in the reaction, and hence, since the rate of reaction depends on the surface concentration, the velocity constant will *rise* towards the end of the reaction. This is the explanation of Bredig's and von Berneck's results. Theoretically, since the reaction is really taking place in the adsorption surface layer, there is no stage at which simple proportionality exists between surface and bulk concentration, and hence no stage at which a true monomolecular velocity constant is to be expected. *Practically*, however, there may be a sufficiently wide range over which the ratio (surface concentration)/(bulk concentration) remains nearly constant, and over this range, therefore, the velocity constant—which is always measured in terms of the bulk concentration—will be approximately constant. It would be a more logical procedure to determine the velocity constant in all cases in terms of the surface concentration of the reactant. If this were done it would probably be found that the velocity constant calculated directly in terms of the surface concentration would be a true monomolecular one, at least over the range at which the concentration of the reactant was not too great. When the asymptotic stage, referred to above, was reached, the velocity would necessarily correspond to a zero molecular reaction, *i.e.* $dx/dt = k$. Whilst this would be the logical procedure it does not appear to have been followed hitherto, because of the difficulty of estimating the surface concentration at various time intervals with sufficient accuracy. At the same time it should not be impossible.

The next point is temperature coefficient. In reactions which are catalysed either by colloidal metals, etc., or by enzymes, the coefficient for a 10° C. rise is at least 2 (*i.e.* the same order as we find for an uncatalysed reaction going on in a homogeneous system). In the cases where solid catalysts are employed, however (such as platinum gauze), the temperature coefficient is much less, being only about 1·3. The following are some examples:—

$$
\begin{array}{llll}
SO_2 + O_2 \rightarrow SO_3 & \text{temperature coefficient}_{10^\circ} & & = 1{\cdot}36 \\
H_2O_2 \rightarrow H_2O + O & \quad ,, & ,, & = 1{\cdot}28 \\
Ti^{\cdots} + H^{\cdot} \rightarrow Ti^{\cdots\cdot} + H & \quad ,, & ,, & = 1{\cdot}29
\end{array}
$$

There is, therefore, a characteristic difference between the behaviour of colloidal (or enzyme) and solid catalysts. This problem might be considered as follows: As often pointed out, it is the slowest of a series of processes, which determines the total rate of the reaction. Now adsorption is known to be an exceedingly rapid process. If now the reacting substances were brought to the surface of the catalyst by capillary forces, the temperature coefficient would correspond to that of the slower process, *viz.* the chemical process in this case. If, on the other hand, the reacting substances are brought to the surface by the slow process of diffusion, for the range of molecular capillary attraction is very small, then the measured velocity would be that of a diffusion process, and the temperature coefficient would be of the low order of 1·5, which we have seen is the case when solid catalysts are used. To account for the high velocity coefficient in colloid or enzyme catalysis, we might consider that the Brownian movement of these particles acted as very efficient stirring—so efficient, in fact, that the diffusion layer was removed as fast as it was formed, with the result that the (homogeneous) chemical action in the adsorbed layer is the real process whose coefficient we measure. One would expect on this view a high temperature coefficient. But does the Brownian movement remove the diffusion layer? Bredig and Teletow (*Zeitsch. Elektrochemie*, **12**, 583, 1906) have calculated the thickness of the layer from the Nernst diffusion expression, *viz.* $K = \frac{OD}{\delta V}$, from the data given by the hydrogen peroxide decomposition in the presence of colloidal platinum, and found that $\delta = 0{\cdot}05$ mm., *i.e.* of the same order as Brunner found in the case of the dissolution of benzoic acid in water. This seems to show that in spite of the Brownian movement the diffusion layer remains unchanged. If this is so, then the above explanation of the high temperature coefficient in the case of colloids and enzymes breaks down. (Unless we indeed assume with Senter that the whole surface of the colloid is not effective, but the effective area increases with temperature rise (Bredig and Teletow assumed it was entirely effective), Senter's reason being the extraordinary sensitivity of colloids to a mere trace of "poison," *e.g.* (HCN).) Senter's view has much in common with that of Langmuir to which we shall refer later. Another attempt at an explanation of the difference in behaviour as regards temperature coefficient is suggested by Denham, as being connected with the fact that the surface energy of a small particle is greater per unit area than the energy of a solid or plane surface, *i.e.* small crystals are more soluble than large ones. Hence the adsorption effects at a colloid particle surface are greater than those at a plane surface such as platinum gauze of the same area; but even if this is so, diffusion, one would think, should be the slowest process present. Capillary forces are only effective over an extremely short range, and though the adsorption is rapid (practically instantaneous) when solute is in the neighbourhood of the surface, the process whereby the depletion of solute is made good must be a diffusion one, and whether the surface energy is high or low seems to have very little to do with it. The ultimate explanation of the difference in the behaviour of colloids and enzymes as distinct from solids, in regard to temperature coefficient of one and the same reaction, is yet to be found.

Some interesting results obtained by Armstrong (*Proc. Roy. Soc.*, **73**, 508, 1904) on the subject of enzyme (lactase) action upon milk-sugar hydrolysis, must be mentioned in connection with heterogeneous catalysis, and especially from the standpoint of the adsorption or physical theory of the same. Armstrong showed that when concentrated milk-sugar solution is hydrolysed with small quantities of lactase, the hydrolysed *mass*, at a given time (46 hours), even in solutions of very different concentration, was *the same* and in no way proportional to the sugar concentrations, as the Law of Mass Action would lead one to expect. He found—

Initial Concentration of Milk Sugar.	Per Cent. Hydrolysed in 46 Hours.	Absolute Mass of Sugar Hydrolysed.
10 per cent.	22·2	2·22
20 ,, ,,	10·9	2·18
30 ,, ,,	7·7	2·21

In dilute solution, on the other hand, in which the enzyme was present in large amount compared with the amount of sugar, Armstrong found that the percentage hydrolysed was strictly proportional to the sugar concentration.

Initial Concentration of Milk Sugar in 100 c.c. Solution.	After Three Hours, Quantity of Sugar Hydrolysed.	Velocity Constant (Monomolecular).
1·0 gram.	0·185 gram.	0·0296
0·5 "	0·098 "	0·0298
0·2 "	0·0416 "	0·0337

It was shown by the writer (*Phil. Mag.*, April, 1909) that a 6 per cent. *cane*-sugar solution has a small effect upon the interfacial tension, oil/water, and Freundlich has shown in agreement with this, that bodies containing hydroxyl are positively adsorbed (though not strongly). This means that in sugar solutions at high bulk concentration a state at the surface is reached which corresponds to surface saturation, the surface concentration remaining practically the same even when the bulk concentration is largely increased. The quantity of sugar hydrolysed in Armstrong's experiments depends on the adsorbed quantity, and, as we have seen, this is practically independent of the bulk concentration changes (when there is considerable sugar present), and hence one can see, on the adsorption theory, a very plausible basis for the rather remarkable observations made in the case of strong solutions of milk sugar in presence of a given limited amount of enzyme. Hudson (*Journ. Amer. Chem. Soc.*, **30**, 1160, 1564, 1908) obtained similar results in the hydrolysis of cane sugar with invertase. If this view is the correct one, the greater the adsorption capacity of the substance the more marked will be the divergence from the mass action principle, *i.e.* the rate of decomposition should be $\frac{dx}{dt} = k$ over a considerable range of ***bulk*** concentration. It is assumed here that the chemical reaction and not the diffusion part of the process is the important thing.

Recently the mechanism of enzyme action has been investigated by Nelson and Vosburgh (*Journ. Amer. Chem. Soc.*, **39**, 790, 1917), the case in point being the action of invertase—in presence of a known amount of $H^{\cdot}$ ion—in bringing about the inversion of sucrose. In the first place it is shown (Nelson and Griffin, *Journ. Amer. Chem. Soc.*, **38**, 1109, 1916) that invertase adsorbed by charcoal or aluminium hydroxide has the same catalytic effect as the same amount of invertase in solution. This is an important and unexpected result. It would be very desirable to know if it were a general property of enzymes. It indicates pretty clearly that Brownian movement is of little or no significance for the phenomenon, since it is not to be expected that adsorbed invertase would still be in rapid translational motion. The general results obtained in the investigation referred to are:—

1. The velocity of inversion of the sucrose is directly proportional to the concentration of the invertase.

2. The velocity is nearly independent of the concentration of the sucrose in the more concentrated sucrose solutions, whilst in very dilute sucrose solutions the velocity increases with the increase of concentration of the sucrose, and finally reaches a maximum.

3. Adsorption is one of the controlling factors in the kinetics of invertase action, and the velocity of inversion curve, where the concentration of sucrose is used as abscissa, has the same general shape as adsorption curves as suggested by V. Henri (*Zeitsch. physik. Chem.*, **51**, 27, 1905).[1]

If these conclusions hold good in other cases as well, the problem of enzyme action will be defined at least with some degree of precision; its inner mechanism—as will be appreciated from the somewhat unsatisfactory nature of the account given in the foregoing pages—is still obscure. The points upon which we want much more light are: the actual significance of the Brownian movement; the significance of diffusion (especially in view of Langmuir's theory which is considered in the following section); the significance of the temperature coefficient, which appears to have its normal (large) value in the case of colloids and enzymes, but a low value in the case of catalysis by massive solids; the mechanism of the poisoning effect; and the reasons for the existence of an optimum concentration of, say, H˙ ions in enzyme effects.

LANGMUIR'S THEORY OF EVAPORATION, CONDENSATION, ADSORPTION, AND HETEROGENEOUS REACTION VELOCITY AND CATALYSIS.

These subjects have been investigated by Irving Langmuir during recent years both from the theoretical and experimental standpoint. A summarising paper published by him (*Journ. Amer. Chem. Soc.*, **38**, 2221, 1916) contains a résumé of these investigations and is reproduced briefly here, mainly in Langmuir's own words.

The fundamental idea underlying Langmuir's theory is the extension of the Braggs' work upon crystal structure (*cf.* Chap. II.) to chemical processes. The surface of a solid is treated from the standpoint of the arrangement of the atoms constituting the surface, surface effects being in general attributed to the residual affinity possessed by the atoms. The surface is regarded as a checker board upon which atoms or molecules of gases may be condensed by being united to certain atoms present in the surface itself. It is essentially a chemical view of the mechanism of such phenomena as adsorption and catalytic effects, in which the adsorbed gas molecules occupy quite definite positions, in some cases the surface being almost entirely covered or saturated, in others only a small fraction of the whole surface being thus occupied. The investigation deals in the first place with crystalline surfaces such as the surface of a metal. As a starting point we may consider very briefly the problem of the atomic vibrations of a metal especially of the atoms in the surface layer.

---

[1] It is worth while noting that Henri regards the enzyme itself as containing some of the medium (water), (*cf.* Farrow's view of colloidal soap, Chap. VIII.).

The atoms in a solid are constantly vibrating over a fixed centre of gravity with a certain average frequency, the frequency being the reciprocal of the time taken to complete a single vibration. The higher the temperature the greater the amplitude of vibration. Let us imagine all the atoms in the surface layer to have their temperature raised suddenly by a given amount. This layer will rapidly cool and will approach the temperature of the underlying layers. The rapidity with which the temperature equalisation takes place will measure the rate at which the movement of one atom affects the adjacent ones. A simple approximate calculation (Langmuir, *Phys. Rev.*, **8**, 149, 1916) gives for the time necessary for the temperature increment of the surface layer to fall to 37 per cent. of its initial value—

$$t_r = \frac{3k}{hd} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the gas constant reckoned per molecule, not per gram-mole, h is the heat conductivity of the solid, and d is the distance between adjacent atoms. The quantity t_r is analogous to Maxwell's "time of relaxation" in a gas which is the time needed for any abnormal distribution of kinetic energy among gas molecules to subside to $1/\epsilon^{th}$ of its original value. For copper we thus find $t_r = 4{\cdot}6 \times 10^{-16}$ seconds. This has been calculated on the assumption that each atom can receive heat from one direction only. When we consider that a single atom in the interior may receive energy from six directions, the time of relaxation of a single copper atom is about 10^{-16} seconds. Now the atomic frequency is approximately $5{\cdot}6 \times 10^{-12}$, or the time necessary to complete a single oscillation is $1{\cdot}8 \times 10^{-13}$ seconds. Thus the time required for an atom nearly to reach temperature equilibrium with its neighbours is only $\frac{1}{1800}$th of the time of an oscillation. This indicates that motions of a single atom must always be very highly damped. In other words, *the atoms behave towards each other as though they were almost completely inelastic.* This inelasticity of the atoms of solids is of great importance in the theory of evaporation and adsorption.

It is known that the effective range of atomic and molecular forces is exceedingly small, probably of the order 10^{-7} to 10^{-8} cms. The smallness of this range compels us to conclude that, in general, the distances through which the surface atoms are shifted from their original positions in the solid are small compared with the average distance between atoms. We must also conclude that the abnormal surface arrangement is usually limited to the surface layer only. This surface layer, according to Langmuir, does not consist of several layers of atoms in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapour. Instead, the change from solid to gas is abrupt. The reason for this is the fact that it is only the gas layer one molecule or atom thick which is held sufficiently firmly to the surface. This fact is fairly well demonstrated by some of the experimental results which will be referred to later. As already mentioned the surface is to be regarded as a sort of checker board containing a definite number of atoms, of definite kinds arranged in a plane lattice formation.

The next point to be considered is the mechanism of vaporisation and condensation of a vapour at the surface of a solid.

When a crystal is in contact with its own saturated vapour the vapour must be continually condensing on the solid while the solid is evaporating (subliming) at an equal rate. The rate at which the molecules of the vapour come into contact with the surface of the solid is given by an equation deduced by Langmuir (*Phys. Rev.*, **2**, 331, 1913). The equation is—

$$m = \sqrt{\frac{M}{2\pi RT}} \times p \quad . \quad . \quad . \quad . \quad (2)$$

where M is the molecular weight of the vapour, R is the gas constant, p is the pressure of the vapour and m is the rate at which the gas molecules strike against the surface, expressed in grams of vapour per square cm. per second.

When a molecule strikes a surface it may be reflected or it may condense, that is, may be held by attractive forces so that it forms at least temporarily a part of the solid body. It is very important to know what fraction of the molecules striking a surface are reflected. In this connection we must bear in mind the conclusion already reached regarding the inelastic nature of collisions. In so far as they are inelastic the collision results in condensation.[1] We may picture the process in the following way:—

The mean free path of the gas molecules at atmospheric pressure is of the order 10^{-5} cm. When a vapour molecule, approaching the surface, comes within a distance of about 2×10^{-8} cm. of the surface layer of atoms it begins to be acted on by the electro-magnetic field close to the surface. As it moves closer to the surface the attractive force increases rapidly and reaches a maximum value. The attractive force then rapidly decreases and falls to zero when the molecule has travelled a distance of about $0{\cdot}6 \times 10^{-8}$ cm. beyond the point at which the attractive force was a maximum. The point at which the attractive force is zero may be regarded as the position of equilibrium. The kinetic energy of the molecule will in general carry it some distance further, but it now encounters repulsive forces of great magnitude. It will then pass once more through the equilibrium position and if its kinetic energy is great enough will escape, that is, the molecule is reflected. In general, however, owing to the inelastic nature of the collision, the energy of the molecule will be dissipated rapidly and it will not escape, that is, it condenses. We have seen that in the interior of crystals the time taken for adjacent atoms to reach thermal equilibrium with each other is of the order 10^{-16} seconds. The duration of a collision between a molecule and a surface, that is, the time between successive passages through the region of maximum attractive force, is of the order 10^{-13} seconds. Thus in general the energy delivered to the incident molecule by the attractive forces is practically wholly dissipated to the adjacent atoms by the time the molecule first reaches the equilibrium position. *The condensation of a vapour on a solid surface thus takes place independently of the temperature of the surface.* This is not in contradiction to experience, for what we ordinarily observe is the difference between the rate of condensation and evaporation.

---

[1] Langmuir considers this question of inelastic collision in the *Physical Review* **8**, 149 (1916).

If practically every molecule of vapour which strikes a surface condenses, it is not at first evident how the molecules are able to arrange themselves to form a crystalline mass. We have to distinguish two extreme cases which may be termed irreversible and reversible sublimation respectively.

By irreversible sublimation is meant that type which occurs, for instance, when a tungsten filament is heated to a high temperature in a well-evacuated bulb. Under these conditions there can be no equilibrium, for the bulb itself is at a temperature thousands of degrees lower than that at which the vapour is produced. The vapour condenses upon the cold surface of the bulb. The vapour is therefore enormously superheated with respect to this surface.

By the term reversible sublimation is meant that which takes place, for example, when iodine or naphthalene is sublimed slowly at ordinary temperatures. In this case we are dealing with small differences of temperature, and under these conditions sublimation and condensation are going on at almost equal rates.

In irreversible sublimation the vapour molecules remain where they first strike the cold surface, being neither reflected nor re-evaporated. The deposit is therefore uniform and wholly *noncrystalline*, since the distribution is merely the effect of chance. By means of this irreversible sublimation it is thus possible to obtain any volatile body in the amorphous form when it condenses.

We have seen that the *condensation* of vapours on a solid body takes place at a rate which is practically independent of the temperature. The rate of *evaporation*, however, increases rapidly with the temperature. When a solid is in equilibrium with its own vapour, condensation and evaporation are occurring simultaneously at equal rates. We have seen that we are justified, in the majority of cases, in considering that all the molecules of vapour which strike a surface are condensed. Now the rate at which the molecules strike the surface is given by equation (2), *viz.*:—

$$m = \sqrt{\frac{M}{2\pi RT}} \times p.$$

Since all the molecules condense, and since the rate of evaporation must be equal to the rate of condensation, we may use this equation to calculate the rate of evaporation m, in terms of the pressure p of the saturated vapour. If condensation and evaporation go on independently of one another, then the equation gives a means of calculating the rate at which a solid evaporates into a perfect vacuum. This relation between the rate of evaporation and vapour pressure was first obtained by Hertz (*Ann. Physik.*, **17**, 177, 1882). For the case of a clean surface of liquid mercury evaporating into a good vacuum, Knudsen (*Ann. Physik.*, **47**, 697, 1915) has proved experimentally that the equation gives the actual rate of evaporation.

Rate of Adsorption of Gases by Solids.

In the process of condensation, if any of the molecules are condensed there must be a time lag before they can re-evaporate. This will bring about a higher concentration of the molecules at the surface than in the body of the gas. In the condensation of a vapour we have seen that the collisions are inelastic, so that every molecule striking the surface condenses. The reasons which have led to this conclusion apply with nearly equal weight to gas molecules of almost any kind striking any surface. It may be observed that hydrogen gas at room temperature suffers considerable reflection. Its behaviour is, however, exceptional. We may now use a modified form of equation (2) to deal with this accumulation of gas at the surface which Langmuir identifies with the phenomenon of adsorption (*cf.* Vol. II., Chap. XI.). Let μ represent the number of *gram-molecules* of gas which strike each sq. cm. of surface per second. It follows from equation (2) that

$$\mu = 43{\cdot}75 \times 10^{-6} \frac{p}{\sqrt{MT}} \quad . \quad . \quad . \quad . \quad (3)$$

The rate at which gas condenses on the surface will then be $a\mu$, where a is a quantity usually very close to unity, and never exceeding unity. If the surface is that of a crystal, there will be a definite number of spaces, N_0, on each square cm. of surface capable of holding adsorbed gas molecules. The forces acting between two layers of gas molecules will usually be very much less than that between the crystal surface and the first layer of molecules. The rate of evaporation in the second layer will, therefore, be generally so much more rapid than in the first, that the number of molecules in the second layer will be negligible. When a gas molecule strikes a portion of the surface already covered, it thus evaporates so quickly that in effect it is equivalent to a reflection. Therefore the rate of condensation of the gas on the crystal surface is $a\theta u$, where θ represents the fraction of the surface which is bare. Similarly the rate of evaporation of the molecules from the surface is equal to $\nu_1\theta_1$, where ν_1 is the rate at which the gas would evaporate if the surface were completely covered, and θ_1 is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a solid surface these two rates must be equal. That is

$$a\theta\mu = \nu_1\theta_1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Also
$$\theta + \theta_1 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Whence
$$\theta_1 = \frac{a\mu}{1 + a\mu} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The quantity θ_1 is a measure of the amount of gas adsorbed. It should be noted that for low pressures the amount of adsorbed gas is proportional to the pressure, but as the pressure increases θ_1 increases more slowly and finally the surface becomes saturated ($\theta_1 = 1$). These relations are in good qualitative agreement with known facts. It will be observed that equation 6 gives the amount of adsorption on a plane crystal surface. No reliable quantitative experimental data seem to be available for the adsorption of gases on such surfaces. The adsorption by glass and charcoal will be considered later.

With a gas such as nitrogen in which the atoms are very thoroughly saturated there is only a feeble field of force around the molecules. When a molecule of nitrogen strikes a surface it is only held by weak secondary valencies. In the general case, therefore, the magnitude of the forces giving rise to adsorbed films will vary over a wide range. The adsorption will therefore exhibit a specific or chemical character according to the nature of the surface and the nature of the gas.

Langmuir has found that *atomic* hydrogen produced by heating a metallic wire in dry hydrogen at very low pressures has a remarkable tendency to be adsorbed on surfaces. Langmuir uses this fact as an argument in favour of the chemical view of adsorption, *i.e.* that the phenomenon is due to valency, for on purely physical considerations one would expect a gas of such low density to be only slightly adsorbed. Experiment has shown also that this adsorbed layer of atomic hydrogen is very stable, for even in the highest vacuum quantities of hydrogen as large as 0·01 to 0·03 c.c. reckoned at atmospheric pressure were adsorbed on cold glass. Langmuir regards this stability as being due to the unsaturated chemical affinity of the atomic hydrogen. Langmuir has also calculated that the amount of atomic hydrogen adsorbed corresponds to a layer of just one atom deep.

Similar results have been obtained by Langmuir in the case of oxygen adsorbed on tungsten filaments. Thus it has been shown that 15 per cent. of all the oxygen molecules striking a tungsten filament at the temperature 2770° abs. react with it to form WO_3. At the same time there is a stable film formed between the oxygen atoms and the tungsten atoms. This persists even at a temperature of 3300° abs. and at very low gas pressure. It is not to be confounded with the WO_3 itself, for the latter is easily volatile and distils from the filament at a temperature 1200° abs. The existence of this oxygen layer on a tungsten filament in oxygen at low pressures shows itself in other ways. Thus a pressure of 0·001 bar[1] of oxygen lowers the electron emission from a filament at 1800° abs. to a very small fraction of its normal value. Also, if a tungsten filament at 1500° abs. is exposed to a mixture of oxygen and hydrogen, the oxygen behaves as though no hydrogen were present. The oxidation of the filament goes on, and during this no hydrogen reacts with the oxygen nor does the hydrogen reduce the WO_3 formed, nor is any atomic hydrogen produced. However, after all the oxygen has been used up the hydrogen *suddenly* begins to disappear by being dissociated into atoms, which then react with the WO_3 previously deposited on the bulb. It is also observed that the electron emission suddenly increases at the same moment at which the hydrogen begins to disappear. We conclude from these results, therefore, that even at an extremely low pressure and at 1500° abs. the surface of the filament is completely covered with oxygen, and that this layer prevents the formation of atomic hydrogen and the normal electron emission. It is evident that the adsorbed oxygen has totally different properties from those we should expect, either with a layer of oxide or a film of highly compressed gas. The facts are in good accord, however, with the view that the oxygen atoms are "chemically" combined with the tungsten atoms. From this point of view the two primary valencies of the oxygen are turned downwards and are saturated by the tungsten, so that a hydrogen molecule striking the surface cannot react with the oxygen and cannot come into contact with the tungsten. The hexavalent tungsten atoms on the other hand are not saturated by the oxygen, so that they are held firmly to the underlying layer of tungsten atoms. Only when the tungsten atoms on the surface become saturated by taking up two other oxygen atoms do they cease to be held to the other tungsten atoms and thus evaporate off as WO_3.

---

[1] One bar = 1 dyne per $cm.^2$ One mega bar = 10^6 bars = one atmosphere *approximately*.

The action of oxygen in preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a catalytic poison (*cf.* p. 455). Langmuir has shown that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the tungsten surface. The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface forming a very stable film.

The poisoning effect of oxygen may also be shown in other ways. Thus when a tungsten filament is heated in a mixture of carbon monoxide and oxygen, the tungsten is oxidised just as if no CO were present. Mixtures of methane and oxygen at low pressures do not react with one another in contact with tungsten at 1500° or even 1800° abs., but the tungsten is oxidised to WO_3 as in previous cases. In the absence of oxygen, methane is gradually decomposed, setting free hydrogen, while the carbon is taken up by the tungsten filament, forming a solid solution. If now oxygen be admitted the oxygen reacts with the carbon in the filament forming CO, and, until all the carbon in the surface layers has been removed, the oxygen does not react with the tungsten. This suggests that when carbon is taken up by tungsten some of the carbon remains as an adsorbed layer of carbon atoms.

Dry ammonia at low pressures is decomposed by a tungsten filament fairly rapidly at 1000° abs. In presence of small amounts of oxygen tungsten cannot decompose ammonia even at 1200° abs. At 1300° abs. the tungsten oxidises to WO_3 just as if the ammonia were absent. Again, the effect may be ascribed to the adsorbed layer of oxygen, one atom in thickness.

In the case of mixed oxygen and cyanogen it has been observed that using a tungsten filament at 1500° abs. the oxidation of the tungsten is largely prevented until the cyanogen has been slowly oxidised to carbon monoxide and nitrogen. If there is an excess of oxygen this then reacts with the tungsten when the supply of cyanogen is used up. Any excess of cyanogen is decomposed by the filament giving nitrogen, the carbon being taken up by the tungsten. Thus cyanogen may be regarded as having a stronger poisoning effect on tungsten than oxygen has. It is well known that cyanogen poisons the catalytic activity of platinum. Experiments at low pressures demonstrate this.

A platinum filament at a temperature of 600° abs. causes carbon monoxide and oxygen to combine rapidly, the carbon monoxide itself acting as a catalytic poison (Langmuir, *Journ. Amer. Chem. Soc.*, **37**, 1163, 1915). At 900° abs. the poisoning effect of the CO disappears and the velocity of the reaction becomes exceedingly great. If, however, a trace of cyanogen is added to the mixture of oxygen and carbon monoxide at a pressure of 10 bars, the catalytic action of the platinum disappears completely even at 900° abs. By raising the temperature to about 1000° abs. the cyanogen reacts with the oxygen to form nitrogen and carbon monoxide. As soon as the cyanogen is all oxidised the catalytic activity of the platinum is restored and the oxygen and CO react rapidly to give carbon dioxide.

The catalytic effect of platinum on the reaction between oxygen and hydrogen is also poisoned by traces of cyanogen. If the temperature of the platinum be raised, the cyanogen and hydrogen react to form hydrocyanic acid.

The fact that these low pressures of cyanogen or oxygen can exert such a powerful poisoning effect is proof that adsorbed films of great stability are formed, films in which the rate of evaporation of the adsorbed molecules is remarkably low. *The effect of these poisons is thus to cover up the active surface.*

Water vapour has the same effect as oxygen in poisoning the catalytic activity of tungsten. A partial pressure of 0·4 bar—the vapour pressure of water at $-78°$ C.—is sufficient to prevent the dissociation of hydrogen by a tungsten filament at 1500° abs.

An idea of the stability of the adsorbed film of oxygen referred to in some of the cases mentioned above will be gathered from the fact that in order to remove it, the filament must be heated in a good vacuum for about half an hour at a temperature of 2300° abs.

The anticatalytic effects of various gases described above are exhibited also by their effect upon the electron emission from the filament. In every case with tungsten, chemically inert gases have been found to be without effect on the electron emission, whereas nearly all gases which combine with the tungsten lower the emission. It is reasonable to ascribe this effect also to the adsorbed layer. Thus oxygen markedly lowers the electron emission, as also does water vapour. On the other hand, carbon dioxide which is not a catalytic poison has no effect on the emission. Krüger and Taege (*Z. Elektrochem.*, **21**, 562, 1915) have studied the effect of catalytic poisons on the photo-electric activity of platinum using ultra-violet light. They find that minute traces of H_2S, HCN, or CO very greatly decrease the photo-electric electron emission.

The effect of poisons on the activity of catalysts is essentially the same with gases at atmospheric pressure as at lower pressures. The above reasoning should therefore apply. At still higher pressure the surface may become entirely covered, that is saturated, and further amounts of the gas have no additional effect. This is stated by Langmuir to be in agreement with experiment. If the gas considered is actually saturated the surface layer may become several molecules thick.

So far we have been considering metallic surfaces. We have now to consider a surface of a somewhat different kind, namely, a glass surface.

Experiment shows that the amount of moisture taken up by a glass surface, is greatly in excess of the amount required to form a layer one molecule deep. Langmuir offers an explanation of this on the assumption that the moisture actually penetrates into the glass. In this sense therefore it is not true adsorption, if we use the term for a pure surface effect. Dried jellies can absorb large quantities of moisture, and dehydrated salts usually absorb moisture even when no definite hydrates are formed. The absorption of the moisture may therefore be regarded as a process of solution of the water by the glass. Ihmori's experiments show that water vapour cannot penetrate into a clean metal. If, however, a layer of oxide is present a great deal more water vapour may be taken up than corresponds to a layer one molecule thick. In the case of charcoal it is quite impossible to say what the true surface area is. McBain's measurements indicate a true adsorption effect followed by a process analogous to a solution.

Equations (4), (5), and (6) cannot apply to adsorption on charcoal. The real reason for this is that we can no longer assume in the case of charcoal that the rate at which the adsorbed gas evaporates from the surface is proportional to the amount present on the surface.

Kinetics of Heterogeneous Reactions.

Langmuir's theory and experimental work leads to the following general conclusion: In a heterogeneous chemical reaction the activity of the surface depends in general upon the nature of, the arrangement of, and spacing of the atoms forming the surface layer.

According to this view, the velocity of reactions in general is not limited by the rate of diffusion through an absorbed film, but by the rate at which the molecules strike—equation (2)—against that portion of the surface which is active. Cases are known, such as the rusting of iron, in which the chemical reaction is determined by the diffusion of a gas through moderately thick films, but such cases are distinct from the typical catalytic reactions in contact with a surface.

This view of heterogeneous catalysis can be put in a quantitative form. The first point is that the velocity of the reaction depends on the fraction of the surface which is covered by adsorbed atoms or molecules. This in turn depends on the rate of condensation and of evaporation of the adsorbed substance.

Consider the surface upon which condensation occurs and suppose that it contains a definite number N_0 of elementary spaces per unit area. Let θ be the fraction of these spaces that are *un*occupied, and θ_1 be the fraction occupied by the adsorbed atoms or molecules. If each molecule condensing requires only one elementary space, the rate of condensation will be equal to $a\theta\mu$ (*cf.* equation (3)). But it may happen that each molecule requires two such spaces before condensation can occur. The chance that one space is vacant is θ, the chance that two given spaces will be vacant simultaneously is θ^2. That is, in the latter case the rate of condensation would be equal to $a\theta^2\mu$. In general, the rate of condensation will be $a\theta^n\mu$, where n is an integer. If a molecule occupies one elementary space its rate of evaporation will be $\nu_1\theta_1$. If two atoms must lie in adjacent spaces in order that they may leave the surface together as a molecule, the rate of evaporation will be $\nu_1\theta_1^2$.

Chemical reactions may take place either between adjacent atoms on the surface or may occur when gas molecules strike molecules or atoms already on the surface. In the former case the velocity of the reaction, in general, is proportional to $\theta^n\theta_1^m\theta_2^p$, where θ_1 and θ_2 are the fractions of the surface covered by the reacting substances and n, m, and p are integers. The reason for the occurrence of the factor θ^n in this expression is that the number of elementary spaces occupied by the products of the reaction may be greater than that occupied by the reacting substances. The reaction according to Langmuir will therefore only occur when vacant spaces are available. We have now to apply these considerations to some actual cases.

There are two types of cases to consider. First, those in which the adsorbed film covers only a small fraction of the surface, *i.e.* $\theta = 1$. Secondly, those in which the surface is nearly completely covered by the adsorbed film.

First Case. Surface only covered to a slight extent.—Let us consider a single gas which undergoes a chemical change, for example, dissociation, in contact with a solid body. The rate of condensation on the surface will be $a_1\mu_1$ and the rate of evaporation of the unchanged gas will be $\nu_1\theta_1^n$, where n represents the number of elementary spaces occupied by each molecule of the substance while on the surface. Then, since the adsorbed film is in equilibrium with the surrounding gas, we have—

$$a_1\mu_1 = \nu_1\theta_1^n \quad . \quad . \quad . \quad . \quad (7)$$

It will be observed that this equation becomes identical with equation (4) when $n = 1$ and $\theta = 1$. The adsorption equation (6) therefore only applies to the case in which a molecule occupies a single space. Equation (7) shows that when $n = 2$, the amount of gas adsorbed is proportional to the square root of the pressure, even at low pressures, *i.e.* θ_1 is proportional to $\mu_1^{1/n}$.

Now the product of the chemical reaction is formed from the adsorbed film by the combination of the substance from m adjacent spaces. In the case of a dissociation m will be unity. If w represents the velocity of the chemical change, which is assumed to be slow compared to the rate at which condensation or evaporation occur, we have—

$$w = \nu_2\theta_1^{m} \qquad (8)$$

Combining equations (7) and (8) we obtain :—

$$w = \nu_2\left(\frac{a_1\mu_1}{\nu_1}\right)^{m/n} \qquad (9)$$

The velocity of the reaction thus varies with the m/n power of the pressure p of the gas. In the case of dissociation of hydrogen molecules by a heated wire, we have $m = 1$ and $n = 2$, so that the velocity at which the gas is dissociated is proportional to the *square root* of the pressure of molecular hydrogen. The recombination of hydrogen atoms in contact with a heated wire takes place in proportion to the *square* of the pressure of the atomic hydrogen. These conclusions are borne out by experiment.

Bodenstein and Ohlmer (*Zeitsch. phys. Chem.*, **53**, 175, 1905) have found that the velocity of the reaction between carbon monoxide and oxygen in presence of heated crystalline quartz is proportional to the pressure of the CO and the *square root* of the pressure of the oxygen. Now if we assume that each carbon monoxide molecule occupies one elementary space while each oxygen molecule occupies two, *i.e.* is present on the surface in the form of atoms, we obtain—

$$\left.\begin{aligned} a_1\mu_1 &= \nu_1\theta_1 \\ a_2\mu_2 &= \nu_2\theta_2^2 \\ w &= \nu_3\theta_1\theta_2 \end{aligned}\right\} \qquad (10)$$

where the subscript 1 refers to CO, 2 refers to O_2, and 3 refers to CO_2. These equations give

$$w = k\mu_1\sqrt{\mu_2} \qquad (11)$$

where k is a constant involving a_1, a_2, ν_1, etc. Thus the relation found by Bodenstein and Olmer follows directly from the assumption that the oxygen adsorbed on the surface is present as separate atoms. In an analogous way one can explain the observation made by Bodenstein and Kranendieck that the velocity of decomposition of ammonia by heated quartz glass is proportional to the square root of the pressure. It will be noted that in this instance Langmuir is extending his theory to the surface of a super-cooled liquid.

The velocity of gas reactions is frequently proportional to the square root of the pressure. According to the Bodenstein-Fink view (*cf.* p. 452) such square root relations are to be explained by diffusion through films whose thickness varies in proportion to the square root of the pressure. There is definite experimental evidence in the case of dissociation of hydrogen molecules, which gives the square root relation, that the film only covers a small part of the surface and is only one atom deep. Hence Bodenstein's theory cannot apply in this case, and it is probable that in general the square root relations are not due to diffusion.

Second Case. Surface nearly completely covered.—Let us consider a reaction in which two gases are in contact with a solid body. One of the gases, which we shall distinguish with the subscript 1, is present in such quantity and evaporates so slowly from the surface that the surface remains nearly completely covered by an adsorbed film of this substance. A second gas 2 undergoes a chemical change when its molecules come into contact with the *un*covered surface. This reaction may be of several kinds. For instance, the gas molecules condensing in vacant spaces may dissociate, may react with the underlying solid, or may react with the adsorbed gas in adjacent spaces. The rate at which the first gas will condense is $a_1\theta^n\mu_1$, where n is the number of elementary spaces occupied by each molecule which condenses and θ is the surface fraction of the solid which is bare. The rate of evaporation will be constant ν_1, since the surface is nearly covered. Therefore for equilibrium—

$$a_1\theta^n\mu_1 = \nu_1 \qquad . \quad . \quad . \quad . \quad (12)$$

The rate at which the second gas will enter into reaction will usually be proportional to $\theta\mu$. It is quite possible, however, in some cases that θ may have any integral or even a fractional exponent. We thus obtain for the rate of reaction

$$w = \nu_2\theta\mu_2 \qquad . \quad . \quad . \quad . \quad (13)$$

Combining these two equations we find—

$$w = \nu_2\mu_2\left(\frac{\nu_1}{a_1\mu_1}\right)^{1/n} \qquad . \quad . \quad . \quad . \quad (14)$$

The velocity is thus proportional to the pressure of the gas 2 and inversely proportional to the nth root of the pressure of gas 1.

This relation is found to hold for a considerable number of reactions when a catalytic poison is present.

Thus Fink found for the reaction $2SO_2 + O_2 = 2SO_3$ in contact with platinum that the velocity is proportional to the pressure of SO_2 and inversely proportional to the square root of the pressure of SO_3. This relation follows directly from equation (14) if $n = 2$. We may thus conclude that the platinum surface was practically completely covered by a layer of adsorbed SO_3 in which each molecule of SO_3 required two elementary spaces for its condensation. Fink measured the amount of this gas adsorbed and found it to be of the order of one molecule thick, so that diffusion through a surface layer has in this case no meaning.

Bodenstein and Ohlmer have found that the reaction between oxygen and carbon monoxide in contact with quartz glass takes place at a rate proportional to the pressure of oxygen, and inversely proportional to the pressure of carbon monoxide. That is, the surface is almost completely covered by CO, each molecule of which occupies one elementary space, $n = 1$. Langmuir found the same relation to hold for this reaction at a platinum surface.

An interesting application of Langmuir's theory arises in connection with enzyme action. The rate, under certain conditions, varies in accordance with Schütz's rule. Consider a reaction in which a substance A is converted into B by the action of an enzyme. Let x be the amount of B formed in the time t assuming that $B = O$ at $t = O$. Let E be the amount of enzyme present. Then according to Schütz's rule—

$$x = k\sqrt{Et} \quad . \quad . \quad . \quad . \quad (15)$$

Thus the amount of B formed is independent of the concentration of A, but is proportional to $\sqrt{Et}$.

By squaring and differentiating equation (15) we obtain, if E remains constant—

$$\frac{dx}{dt} = 1/2k^2\frac{E}{x} \quad . \quad . \quad . \quad . \quad (16)$$

Now an enzyme is a colloid on the surface of which a reaction may take place. Schütz's rule thus means on Langmuir's theory that the product B of the reaction practically covers the entire surface of the colloid particle with a layer one molecule thick. By comparing equations (14) and (16) we see that $n = 1$, that is, each adsorbed molecule occupies one elementary space on the surface of an enzyme particle. The reaction therefore takes place on the part of the colloid surface not occupied by the molecules of B. From equation (14), however, we should expect that the velocity of the reaction would be proportional to the concentration of A. This is not the case. Langmuir tentatively suggests that molecules of A are adsorbed over the surface not occupied by B, and that molecules of B can *displace* molecules of A thus adsorbed. Let θ_A and θ_B be the fractions of the surface covered by A and B respectively. Then we have—

$$\alpha_B\theta_A\mu_B = \nu_B\theta_B$$
$$w = \nu_A\theta_A.$$

Since θ_B is nearly unity, we thus have—

$$w = \left(\frac{\nu_A\nu_B}{\alpha_B}\right)\frac{1}{\mu_B} \quad . \quad . \quad . \quad . \quad (17)$$

which is of the same form as equation (16) and is thus in agreement with Schütz's rule.

Whilst it is readily seen that the rate of reaction is proportional to θ_A there does not appear to be any good reason for identifying the proportionality factor with ν_A. This point is discussed by Moelwyn-Hughes, Pace and Lewis (*J. Gen. Physiol.*, 1929).

As already pointed out, the distinctive feature of Langmuir's theory is the importance which is attached to the orientation of the molecules composing the surface layer, and the significance of residual affinity as being the origin of effects hitherto regarded as physical, *i.e.* non-specific in the chemical sense. Langmuir has extended these ideas to the structure of the surface layer of liquids, the phenomena of surface tension, spreading of liquids and adsorption upon liquid surfaces. This forms an essentially chemical view of capillarity. It may be considered conveniently in this place, as the conclusions arrived at have a direct bearing upon the mechanism of reactions at surfaces. It also bears directly upon certain aspects of colloidal systems (*cf.* Chap. VIII., Vol. I., and Chap. XI., Vol. II.).

In the brief account which follows we shall again employ Langmuir's own words to a large extent.

THE "CHEMICAL" THEORY OF CAPILLARITY AND ADSORPTION.

Since the time of Laplace surface tension has been regarded as a purely physical phenomenon. The forces of attraction were regarded as purely functions of the distance of the molecules apart, the force being the same in all directions around any molecule inside a mass of fluid. Within the last few years, however, quite different conclusions have been arrived at regarding the ultimate origin of capillary effects. The new view is essentially due to two independent investigators, Langmuir (*Met. Chem. Eng.*, **15**, 468, 1916; *J. Amer. Chem. Soc.*, **39**, 1848, 1917) and Harkins (*J. Amer. Chem. Soc.*, **39**, 354, 541, 1917). Although this view involves a radical change in our mode of regarding capillary effects it must be borne in mind that any *thermodynamic* relation, such as the adsorption equation of Gibbs (which involves surface tension and was deduced many years prior to the enunciation of the chemical view of capillarity), retains its full significance, because thermodynamical reasoning is quite independent of any molecular theory respecting the mechanism of the phenomenon concerned (Gibb's equation is considered in Chap. XI., Vol. II.).

According to the chemical or valency theory of capillarity, surface tension is due to residual affinity, as a result of which the molecules in the surface layer are orientated in definite positions. The structure of the surface layer of atoms is regarded as the principal factor in determining the magnitude of the surface tension or rather the surface energy of liquids. This conclusion is supported by the available data on the surface tension of organic liquids. According to the theory the molecules arrange themselves in the surface layer in such a way that their active portions, *i.e.* the portions possessing much residual affinity, are drawn *inwards*, leaving the least active portions of the molecule to form the surface layer. Chemical action may be assumed to be due to the presence of electromagnetic fields surrounding atoms. Surface tension or surface energy is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms.

The molecules in the surface layer arrange themselves so that this stray field is a minimum.

The surface energy of a liquid is thus not a property of the molecule as a whole, but depends only on *the least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer.

In liquid hydrocarbons of the aliphatic series the molecules arrange themselves so that the methyl groups at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same no matter how long the hydrocarbon chain may be. As a matter of fact. the surface energy of all these different substances from hexane to molten paraffin have substantially the same surface energy, namely, 46 to 48 ergs per cm.^{2}, although the molecular weights differ very greatly. In the case of the alcohols, CH_3OH, C_2H_5OH, etc., it is found that their surface energies are practically identical with those of the hydrocarbons. This would be expected if the surface layer consisted of the alkyl groups, the hydroxyl groups all being directed inwards. Particularly interesting relations are found in the case of the benzene derivatives. In benzene itself the molecules arrange themselves so that the benzene rings lie flat upon the surface, the surface energy of benzene being about 65 ergs per square cm. If an active group, such as OH, replaces one of the hydrogen atoms, as in phenol, this group is drawn into the body of the liquid, apparently tilting the benzene ring up on edge and raising the surface energy to about 75 ergs per square cm., which is taken as corresponding to the perimeter of the benzene ring. Thus *any active group* strong enough to tilt the ring up on edge raises the surface energy to about 75 ergs. Two active groups side by side (ortho-position) have no greater effect than one. Two active groups opposite one another (para-position) cannot both go wholly below the surface, so that the surface energy becomes abnormally large, about 85 ergs in the case of *p*-nitrophenol. The substitution of methyl or ethyl groups in the benzene ring lowers the surface energy except where an active group in an adjacent position draws these groups below the surface.

Evidence for this view of capillarity is also obtained from experiments on thin films of oil on water. The minimum thickness of such a film has been employed by Lord Rayleigh to determine approximately the diameter of a molecule (*cf.* Vol. I., Chap. I.). Extensive measurements have been carried out by Devaux who has determined the areas covered by the oil films from weighed amounts of oil. To do this a dilute solution (1 : 1000) of the oil in benzene is prepared, one or two drops of this solution being placed upon the water surface. The benzene evaporates and leaves the oil. Knowing the volume of the oil added in this manner and the area covered by it, the thickness of the film is readily calculated. Devaux considers that this thickness represents the diameter of the molecule. Thus, in the case of triolein he finds this thickness to be $1{\cdot}1 \times 10^{-7}$ cm. Using Perrin's value for the Avogadro Constant, and knowing the molecular weight and density of triolein, he calculates that the diameter of the molecule of triolein should be $1{\cdot}13 \times 10^{-7}$ cm. This affords considerable evidence that the films are one molecule thick. This conclusion greatly simplifies the problem of explaining the cause of the spreading of oils upon water.

It is natural to assume that the force which causes the spreading of an oil upon water is due to an attraction between the water molecules and the oil molecule. It cannot be the entire oil molecule which is involved, however, as this would mean solubility of the oil and not simply spreading. There must be some portion of the oil molecule which has an affinity for the water molecules. Let us take the case of oleic acid. There is no doubt but that the carboxyl group has a marked affinity for water. The solubility of the organic acids in water, as compared with the insolubility of the corresponding hydrocarbons, is evidence for this. This affinity is probably due to the residual valency of the oxygen atom. On the other hand, hydrocarbons have a greater affinity for one another than for water, as is shown by their mutual miscibility, although insoluble in water. Hence when oleic acid is placed upon water, it is probable that the carboxyl groups dissolve in, *i.e.* combine with, the water. The long hydrocarbon chains have too much attraction for one another, however, and too little for water to be drawn into solution merely as a result of the affinity of the carboxyl group for water. By spreading out so as to form a film just *one molecule thick* all the carboxyl groups can combine with the water without causing the hydrocarbon chains to separate from one another.

The spreading of an oil upon water is thus due to an "active group" in the molecule. This leads directly to the prediction that an oil without active groups, such as a pure hydrocarbon oil, should not spread at all. This is in agreement with experiment. Thus Hardy (*Proc. Roy. Soc.*, **86**A, 610, 1912) found that saturated hydrocarbons of the aliphatic series, as well as benzene, cymene, etc., do not spread. Hardy remarks: "The great chemical stability of the paraffins makes chemical interaction with water impossible. Some degree of chemical action would seem to be necessary to make one fluid spread as a film between two others (air and water)." On the above view of the mechanism of spreading of oleic acid it is concluded that the oleic molecules are orientated, the carboxyl groups being immersed in the water whilst the hydrocarbon chains stand vertically upward. Acetic acid is readily soluble in water because of the great attraction of the carboxyl group for water which overcomes the attraction of the alkyl groups for one another, these being much fewer in number than in the case of oleic acid.

The available data indicate that a double bond increases the solubility of a compound in water. Thus ethylene is more soluble than ethane. Crotonyl alcohol is soluble in 6 parts of water, whilst butyl alcohol requires 12. This suggests that the double bond as well as the carboxyl groups may be drawn into the water surface, if there is only a limited amount of oil on a large surface of water. If the water surface is limited, however, the carboxyl groups may be expected to displace the double bonds. Following out this line of reasoning Langmuir has made a number of determinations of the spreading of various substances upon water, from which he has calculated the average cross-section of the molecules in a plane parallel to the water surface, and likewise the length of the molecule perpendicular to the surface. A few of the results are reproduced :—

Substance.	Cross-section cms.^{2}	$\sqrt{\text{Cross-section.}}$	Length in cms.
Palmitic acid . .	21×10^{-16}	$4{\cdot}6 \times 10^{-8}$	24×10^{-8}
Stearic acid . .	22	4·7	25·0
Cerotic acid . .	25	5·0	31·0
Oleic acid. . .	46	6·8	11·2
Triolein . . .	126	11·2	13·0
Tristearin. . .	66	8·1	25·0

An examination of the results shows that the cross-sections of the molecules vary over quite a wide range, from 21 to 126×10^{-16} cm.^{2} The three saturated acids, palmitic, stearic, and cerotic, all occupy nearly the same areas, notwithstanding the fact that the number of the carbon atoms increases from 16 to 26.

It is evident that the molecules are very much elongated, the length of the palmitic molecule being about 5·2 times its average diameter. The results indicate that the molecules arrange themselves on the surface with their long dimension vertical as is required by the theory. The molecule of tristearin has the same length perpendicular to the surface as the stearic molecule, but three times the cross-section. Thus each of the three active groups has been drawn down to the surface of the water while the hydrocarbon chains are packed in side by side, and are erect upon the surface.

The view of surface structure here developed gives us a fairly definite picture of the phenomenon of adsorption as envisaged from the molecular standpoint. The films of oil or solid fats differ from adsorbed films of gases only by their non-volatility. In view of the results obtained in the spreading of films we should expect that a true reversible adsorption layer, containing the solute at the surface of a solution, should not be more than one molecule thick. Langmuir (*loc. cit.*) discusses the rather scanty data available in connection with this point. The conclusion appears to be borne out in a fairly satisfactory manner. The evidence is, however, by no means complete. Of course such a conclusion cannot apply to cases in which the solute does not remain in true solution but appears to form a gelatinous layer on the surface (*cf.* Lewis, *Phil. Mag.*, 1908 and 1909).

SOME TECHNICAL APPLICATIONS OF CATALYSIS.

It will be readily understood that catalysis necessarily occupies an important place in technical operations, because of the advantages which it possesses in connection with convenient working temperatures, acceleration of production, and diminished cost of upkeep. By way of illustration it is proposed to consider a few cases of catalysis which are already of great technical significance.

As an instance of homogeneous catalysis, mention may be made of the inversion of cane sugar by $H^{\cdot}$ ion, which is accomplished technically by means of carbonic acid when a very pure invert sugar is required, as in wines. Homogeneous catalysis also plays a part in the preparation of viscose (acetyl cellulose), the catalysts being water, $ZnCl_2$, NH_4NO_3, or organic salts (*cf.* Knoevenagel, *Zeitsch. angewandt. Chem.*, **27**, 505, 1914). The Friedel-Craffts' reaction in its various forms is a further illustration of positive catalysis. Negative catalysis is met with in the action of preservatives, *e.g.* the preservation of H_2O_2 by a trace of acid, or cinchonidine (Trimble, U.S. Pat. 1,128,637, 1915), or acetanilide; the prevention of oxidation of chloroform by a trace of alcohol; the preservation of HCN solutions by a trace of HCl or H_2SO_4.

Heterogeneous catalysis, however, is of far greater technical importance than homogeneous catalysis. The Deacon Chlorine process and the Contact Sulphuric Acid process have already been referred to in dealing with equilibrium in gaseous systems. With regard to the latter process, owing to the high cost of platinum, other contact material is now finding application, *e.g.* ferric oxide. This substance has the advantage of being less sensitive to poisons, and when rendered inactive is easily replaced. The optimum temperature in the case of ferric oxide is higher than that in the case of platinum. This is scarcely a disadvantage, for the reaction proceeds very much more rapidly at the higher temperature. It will be observed that ferric oxide is an oxide of a metal which is capable of giving rise to different oxidation stages. Presumably the oxide goes through a cycle of alternate reductions and reoxidations during the catalytic process. In regard to the chlorine process, it may be mentioned that the catalytic effect of the cupric chloride—in so far as purely material changes are concerned—likewise consists in alternate reductions and oxidations, thus—

$$
\begin{aligned}
&2CuCl_2 = Cu_2Cl_2 + Cl_2\\
&Cu_2Cl_2 + O = Cu_2OCl_2\\
&Cu_2OCl_2 + 2HCl = H_2O + 2CuCl_2.
\end{aligned}
$$

In the Hargreaves-Robinson process of salt cake (Na_2SO_4) manufacture from sodium chloride, the stoicheiometric equation is—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

This reaction is accelerated, and the working temperature consequently lowered, by the addition of a little ferric oxide to the salt, or better still by the further addition of a small quantity of copper oxide. It is a remarkable fact that mixed catalysts often, though not always, possess greater activity than the sum of the separate effects, *i.e.* the result is not simply additive.

The most important problem at the present time is, of course, the fixation of atmospheric nitrogen. Several methods have been employed, but we shall restrict ourselves to a very brief consideration of one, namely, the Haber process, which consists in the direct union of hydrogen and nitrogen gases to produce ammonia. The real success of this method depends primarily upon two considerations: (1) the proper choice of a catalyst, for without a catalyst the rate of union of the two gases is far too slow to be of any technical importance, and (2) the employment of fairly high pressures, for the reaction, $N_2 + 3H_2 = 2NH_3$, is accompanied by a diminution in volume, and therefore, the greater the pressure, *i.e.* (the concentration), the greater the percentage yield of ammonia; although of course, the equilibrium *constant* itself is independent of the pressure. At 1000° C. the equilibrium corresponds to almost complete dissociation of the ammonia. Consequently it is essential to work at a much lower temperature. If, however, the temperature be lowered much the *rate* of reaction is enormously diminished, so that, to obtain the optimum working conditions, we must have a precise knowledge of the value of the equilibrium constant at various temperatures, and a knowledge of the velocity constants in presence of various catalysts at corresponding temperatures. Without going into any constructional details, it may be mentioned that the uncombined nitrogen and hydrogen are worked back again into the reaction chamber containing the catalyst, which is maintained at a temperature of 500° to 700° C. The following table indicates the effect of pressure in increasing the *equilibrium amounts* of ammonia at various temperatures:—

Pressure in Atmos.	Equilibrium amounts of NH_3.			
	550° C.	650° C.	750° C.	850° C.
1	0·077	0·032	0·016	0·009
100	6·7	3·02	1·54	0·874
200	11·9	5·71	2·99	1·68

It will be observed how rapidly the equilibrium amount of NH_3 falls as the temperature rises. As regards catalysts, many materials have been tried. At the present time pure iron appears to be that generally employed. Its activity depends upon its method of preparation, *i.e.* upon the nature of the surface exposed, and, further, like heterogeneous catalysts in general, iron is very sensitive to traces of poisons. Thus, if 0·01 per cent. of sulphur be present, the iron is of little use, and if 0·1 per cent. be present, the activity of the iron is nil. Among other poisons are: selenium, tellurium, arsenic, phosphorus, boron, lead, tin, zinc, bismuth, and many carbon compounds. On the other hand, the presence of a mere trace of certain oxides and salts, *e.g.* oxides of the alkali and alkaline earth metals, greatly enhances the activity of the catalyst proper. These are usually spoken of as "promoters". The mechanism of their action is not clear; probably they react with one of the interacting gases (the nitrogen) to form unstable nitrides, though this cannot be a complete explanation, for the iron itself almost certainly forms a nitride which reacts with the hydrogen either directly or indirectly (in the form of nascent nitrogen atoms).[1] Since the catalyst is thus sensitive to traces of impurities, the reacting gases themselves must be produced, not only in quantity, but also in a high state of purity. This constitutes in itself a large technical problem.

As a further instance of catalysis we may cite the Ostwald process for the oxidation of ammonia to nitric acid. The stoicheiometric equation is: $NH_3 + 4O = HNO_3 + H_2O$. The difficulty in this process is to stop the reaction at the nitric acid stage, for the complete oxidation of ammonia would lead to the production of free nitrogen. Finely divided platinum is an excellent catalyst for the nitric acid production, but it is capable also of bringing about the further oxidation of the acid, which must be avoided. The difficulty is surmounted by taking advantage of the fact that the rates of the two reactions are very different, the formation of nitric acid being much more rapid than its further oxidation. Hence by passing ammonia and air at a certain high speed through a plug of the catalyst, a good yield of nitric acid may be obtained.[2] It is obvious that the condition for success in this as in all other cases depends primarily upon a complete physico-chemical examination of the processes occurring in the reacting system.

Finally, we may refer to the recent process of hydrogenation of oils, whereby unsaturated acids, such as oleic, may be converted into saturated acids, such as palmitic, by absorption of hydrogen gas in presence of finely divided metals, such as nickel. In this way the valuable solid fats may be obtained directly from the less valuable liquid oils.

The following is a brief enumeration of a few of the more important catalytic processes not referred to above: the dehydrogenation of a cyclic alcohol such as borneol to form camphor, by passing the alcohol over reduced copper at 150° C.; the "drying" of oils, *i.e.* the oxidation of linseed oil in presence of red lead or manganese dioxide; the dehydration of an alcohol to a hydrocarbon in presence of thoria, alumina, titanium dioxide, or the blue oxide of tungsten; the action of anhydrous aluminium sulphate in the etherification process; the action of metallic sodium as a polymerisation agent in the production of artificial rubber from isoprene; the action of lime (through the hydroxyl ion) in the saponification of fats; the action of mercuric sulphate in presence of sulphuric acid as a powerful catalyst for the oxidation of naphthalene to phthalic acid in the synthesis of indigo; the oxidation of aniline to "aniline black" by atmospheric oxygen by a small quantity of *p*-amido-phenol in presence of a copper salt; surface combustion as in the Bone-McCourt process, incandescent gas mantles, and many other operations and processes of technical importance.

---

[1] Ammonia may be produced by passing the nitrogen and the hydrogen *alternately*, instead of *simultaneously*, over the catalyst; this points to nitride formation. It is a remarkable but unexplained fact, that a *small quantity* of hydrogen must be present in the nitrogen.

[2] Recently iron has been employed as catalyst in this process. The activity of iron is greatly enhanced by promoters such as cerium, thorium, bismuth, tungsten, or copper.

In addition to catalysis, the brief references which have been made to the technical importance of the principle of equilibrium, as a criterion of maximum yield in reaction in liquids and gases, and likewise the numerous technical applications of colloid chemistry and electrochemistry, should serve to impress upon the reader the fundamental significance of physical chemistry for chemical industry.

SUBJECT INDEX.

ABNORMAL substances. *See* Polymerised substances.
Absorption spectra of solutions, 203 *seq.*
Acetic acid, composition of liquid, 98.
— — electrolytic dissociation of, 221.
— — molecular weight of, 97.
"Active" molecules, 410 *seq.*
Addition compounds in catalysis, 416 *seq.*
— of inert gas on equilibrium, effect of, 145 *seq.*
— — one of the reacting constituents on equilibrium, effect of, 146 *seq.*
Adsorption, 326, 339 *seq.*, 344, 346 *seq.*, 348 *seq.*, 350 *seq.*, 353 *seq.*, 365 *seq.*, 374 *seq.*, 457, 459, 461, 465 *seq.*, 474 *seq.*
Ammonia, electrolytic dissociation of, 222.
— synthesis of, 133, 479 *seq.*
— to nitric acid, oxidation of, 480.
Ammonium chloride, electrolytic dissociation of, 225.
— — vapour density and dissociation of, 302-307.
Amphoteric electrolytes, 265-269.
Analytical chemistry, principles of, 315 *seq.*
Anomaly of strong electrolytes, 224 *seq.*
α rays, 50 *seq.*, 449.
Arrhenius' theory of electrolytic dissociation, 183, 194-198.
Arsenic sulphide, coagulation of colloidal, 343.
Association, molecular, in liquids, 96 *seq.*, 180, 294 *seq.*
Atom, constitution of the, 30 *seq.*, 36 *seq.*
— disintegration of the, 50-53.
— inertia of an, 48.
— structure of the, 45 *seq.*, 47 *seq.*
Autocatalysis, 421 *seq.*
"Avogadro Constant," *i.e.* the number of molecules in one gram-molecule, 17 *seq.*, 29, 42-43.
Avogadro's hypothesis, 4, 5, 171 *seq.*, 194 *seq.*

BAR, definition of the, 466.
Barium chloride, electrolytic dissociation of, 218.
Bimolecular reactions, 390 *seq.*
Boiling point law of Ramsay and Young, 92.
— — of solution, rise of, 175, 181.
Boyle's Law and colloidal solutions, 29.
— — deduction of, 4 *seq.*, 167 *seq.*
— — deviations from, 55 *seq.*
Bragg's application of X-rays to the elucidation of crystal structure. *See* Crystal structure.
β-rays, 50 *seq.*
Bredig's method of preparation of colloidal metals, 327, 340.
Brownian movement and molecular reality, 16 *seq.*
— — in gaseous system, 41, 42.
— — or motion, 16 *seq.*, 23 *seq.*, 333, 365, 375.
— — to electronic charge, relation of, 42.
Buffer solutions, 262 *seq.*

CAILLETET-MATHIAS' LAW, 63, 65.
Calorie, 55.
Cane sugar (sucrose), inversion of, 117, 204 *seq.*, 236, 247, 248, 249-250, 388 *seq.*, 411-413, 415, 425, 426, 427, 428, 441, 460 *seq.*, 478.
Capillarity, 96 *seq.*, 371 *seq.*, 460, 461 *seq.*
— "chemical" theory of, 474-477.
Catalysis, dual theory of, 423-429.
— homogeneous, 117, 204 *seq.*, 236, 238, 240, 247-250, 270-273, 388 *seq.*, 406, 407, 413, 414-428, 429-439, 440-443, 478.
— in heterogeneous systems, 130 *seq.*, 139-141, 142 *seq.*, 450-455, 470-474, 478-481.
— — mixed solvents, 440 *seq.*
— negative, 430 *seq.*
— pulsating, 455.
— technical applications of, 477-481.
— theories of heterogeneous, 456-461, 465 *seq.*, 469, 470-474.
Catalytic effect of the undissociated molecule of an electrolyte, 423-429.
— influence of the medium, 429 *seq.*
— poisons, 455, 467-469.
Cataphoresis, 213, 334, 344 *seq.*

"Characteristic" equations or "Equations of State," 68-92.
Charge on electron. *See* Electron.
Charles' or Gay-Lussac's Law, 4 *seq.*
Chlorine manufacture, 133, 138-142, 143 *seq.*, 478.
Clausius' equation, 85-86.
Cohesion or molecular attraction, 7 *seq.*, 57 *seq.*, 71 *seq.*, 78, 86, 87, 372.
Collision frequency between molecules, 7, 409.
— nature of atomic, 462.
Colloidal particles, Brownian movement of. *See* Brownian movement.
— — coagulation of, 342-348, 349-350, 360 *seq.*
— — diffusion of, 330 *seq.*
— — electric charge on, 333-342, 345, 364.
— — in precipitates, 328 *seq.*, 344 *seq.*
— — "molecular weight" of, 331.
— — mutual precipitating action of, 348 *seq.*
— — optical properties, 331, 332.
— — osmotic pressure of, 330, 331.
— — peptisation of, 350-353.
— — protective effect. *See* Peptisation.
— — size of, 332.
— solutions, compressibility of, 29.
— — in general, Chap. VIII.
— — stability of, 328 *seq.*, 341 *seq.*, 346, 371-375.
— — viscosity of, 359-362.
— state, von Weimarn's theory of the, 328 *seq.*
Complex ions, 205, 206.
Compressibility of gases, 72.
Condensation of atoms and molecules on surfaces, 461-474.
— — vapour upon electrically charged particle, 35 *seq.*
Conductivity, electrical, of metals, 44.
— of solutions, electrical. *See* Electrolysis and Electrical resistance.
— thermal, of metals, 44.
Consecutive reactions, 402-406.
Constant of equilibrium. *See* Equilibrium constant.
— Velocity. *See* Rate of reaction.
"Contact" process of sulphuric acid manufacture, 133, 142 *seq.*, 144, 450 *seq.*, 458 472, 478.
Continuity of state, 59, 65 *seq.*, 73 *seq.*
Copper sulphate, electrolytic dissociation of, 218.
Corpuscles. *See* Electrons.
Corresponding states, principle of, 82-84, 88-91.
γ-rays, 50 *seq.*
Critical constants, calculation of, 64 *seq.*, 74 *seq.*, 79, 86, 89, 90.
— data, 60, 63, 65, 79 *seq.*, 89.
— pressure, 59, 60, 63, 79 *seq.*
— temperature, 59, 60, 63, 65, 79.
— volume, 59, 60, 63, 65, 79.
Crystal structure and X-rays, 99-115.
Cube, 100.

DEACON process. *See* Chlorine manufacture.
Decay, law of radio-active, 51.
Degree of electrolytic dissociation, 193 *seq.*
— — freedom (mechanical), 32.
— — — (Phase rule). *See* Phase rule.
Density of a gas, abnormal, 133 *seq.*
— — — substance, limiting, 80.
— — solutions, 201.
Depression of freezing-point, molecular, 179 *seq.*, 183, 196 *seq.*, 201.
Detergent action, 354.
Diameter, law of the rectilinear. *See* Cailletet-Mathias' Law.
— of molecules, 11 *seq.*, 13, 15, 477.
Diamond, structure of the, 113-115.
Diazo-acetic ester, decomposition of, 418 *seq.*, 424 *seq.*, 433 *seq.*
Dibasic acids, ionisation of, 223, 224.
Dielectric capacity of gases, 11.
Dieterici equation of state, 86-92.
Diffraction grating, 106 *seq.*
Diffusion coefficient of electrolytes in solution, 376-383.
— Einstein's theory of, 23-29.
Dihydrol, 98.
Dilute solutions, theory of, 164-183.
Dilution formula of Partington, 228.
— — — Rudolphi, 227.
— — — van't Hoff, 227 *seq.*
— Law of Ostwald, 220 *seq.*, 224, 277.
Disintegration of the atom. *See* Atom.
Dispersion coefficient of a precipitate, 328.
Displacement effect, the, 440-443.
Dissociating media, 156, 198 *seq.*, 274 *seq.*, 278 *seq.*, 442.
— power. *See* Dissociating media.
Dissociation constant, electrolytic. *See* Dilution Law of Ostwald.
— gaseous, 132 *seq.*, 150, 289 *seq.*, 300, 307.
— pressure, 119, 299 *seq.*, 304, 306.
Dissolution of a solid in a liquid, velocity of, 445 *seq.*
Distribution coefficient, 291.
— Law of Nernst, 288 *seq.*, 291-298.
— of atoms in crystals, 99, 115.
— — base between acids, 237-240.

Distribution of molecules in space, 54 *seq.*
— — velocities among molecules, 2 *seq.*
Dodecahedron, 180.
Double-layer, electrical, 10, 334 *seq.*, 373.
Dual theory of catalysis, 423-429.

EIGHTH order reaction velocity, 394.
Einstein's theory of diffusion and Brownian movement, 23-29.
Electric field, effect upon a charged particle, 33 *seq.*, 37, 38-42.
Electrical charge on an electrolytic ion, 30, 41, 42.
— Double-layer. *See* Double-layer.
— osmose. *See* Endosmose.
— resistance of solutions, measurement of, 189, 190.
Electrocapillarity, 371, 373.
Electrochemical equivalence, law of, 189.
Electrolysis, 188 *seq.*
Electrolyte, 181 *seq.*, 188-281.
Electrolytes, diffusion of, 376-383.
Electrolytic dissociation, 155, 156, 188-281.
— — degree of, 193 *seq.*
— — magnitude of, 214-220.
— equilibria, heterogeneous, 308-325.
— — homogeneous. *See* Dilution law of Ostwald.
Electromotive force, 208.
Electron, charge on the, 35-42.
— mass of the, 43.
— ratio of mass to charge on the, 35.
— theory of atoms, 33, 45-50.
Electrons in metals, *rôle* of, 44.
— sources of, 33, 44.
Emulsification, 353-360.
Emulsion particles, electric charge on, 334.
— — size of, 332
Emulsions, 19 *seq.*, 326 *seq.* *See also* Emulsification.
Endosmose, 365-368.
Enzymes, 453, 457, 459-461, 473.
Eötvös-Ramsay-Shields' method of determining molecular association, 96-98.
Equation of state, reduced, 83.
Equations of state, 68-92.
Equilibrium constant, 121 *seq.*, 137, 143, 158, 162, 186, 220 *seq.*, 269, 277, 289, 292 *seq.*, 300 *seq.*, 305, 309 *seq.*, 312 *seq.*
Equipartition of (kinetic) energy, principle of, 18, 32.
Equivalent conductivity, 190, 191.
— — at infinite dilution, 191.
Erg, 55.
Esterification equilibrium, 157-162, 406, 416.
— Goldschmidt's theory of, 435-439.
Ethyl alcohol, molecular weight of, 97.
Evaporation, Langmuir's theory of, 461 *seq.*
Extraction, process of, 296-297.

FERMENTS, inorganic. *See* Inorganic ferments.
Ferric hydroxide, coagulation of colloidal, 343.
— — sign of electric charge on colloidal, 340.
Filament, catalytic effect of metallic, 464, 466 *seq.*
Films, thickness of surface, 10, 14, 447 *seq.*, 458 *seq.*, 462 *seq.*, 474 *seq.* *See also* Double-layer, electrical.
Filtration, 371.
Fixation of nitrogen. *See* Ammonia, and p. 145.
Force of attraction (electrical), 199.
— — — (molecular). *See* Cohesion.
Franz-Wiedemann Law, 44.
Freedom, degree of (mechanical). *See* Degree of freedom.
— — — (Phase rule). *See* Phase rule.
Free energy, 116.
Free path, mean. *See* Mean free path.
Freezing-point, depression of. *See* Depression of freezing-point.
Friction, internal. *See* Viscosity.

GAS constant (R), 12, 17, 31, 55.
— law, 12, 17, 55, 171-174, 178.
Gaseous reactions, heterogeneous, 450 *seq.*, 465, 469, 478.
— — homogeneous, Chap. III., p. 116.
— systems, behaviour of, Chap. II.
Gases, molecular attraction in. *See* Cohesion.
— — diameter of, 15.
— — velocities in, 2 *seq.*, 5.
— specific heat of, 30-32.
— the rare. *See* Rare gases.
— viscosity of, 6, 7.
Gas-liquid heterogeneous equilibria, 292 *seq.*
— solid heterogeneous equilibria, 299 *seq.*
Gay-Lussac's or Charles' Law, 4 *seq.*, 169.
Gelatin, 327, 331, 344, 350 *seq.*, 364, 368.
Gels, 327, 329, 342 *seq.*, 364.
Gibb's adsorption equation, 457.
Glucose, muta-rotation of, 272 *seq.*
"Gold number" of a protective colloid, 350.

"HALF-LIFE" period, 51 *seq.*
Hardy-Schulze Law, 342-348.

Heat of electrolytic dissociation, 206.
— — neutralisation, 206-208.
Heats of a gas, ratio of the two specific, 31 *seq.*
— specific (molecular), of gases, 30 *seq.*
Helium atom, 48 *seq.*, 53.
Helmholtz double-layer. *See* Double-layer.
Heterogeneous catalysis. *See* Catalysis.
— equilibria (gaseous), 288 *seq.*, 299-307.
— — involving ions, 308-325.
— reaction velocity, Chap. X.
Hittorf transport number, 209 *seq.*
van't Hoff's theory of osmotic pressure in dilute solutions, 165-183.
Homogeneous chemical equilibrium, Chaps. III. to VI.
Hydrates in solution, 184 186.
Hydriodic acid gas decomposition, 124 *seq.*, 130 *seq.*, 145 *seq.*
Hydrochloric acid, electrolytic dissociation of, 217.
Hydrogen atom, mass of, 43.
— molecule, mass of, 43.
— peroxide, decomposition of, 453, 455, 458.
(Hydrol) monhydrol, dihydrol, trihydrol, 98.
Hydrolysis of esters. *See* Esterification equilibrium. *Cf. also* pp. 271, 390, 411, 425, 432, 440-443. *See also* Decomposition of diazo-acetic ester.
— — salts, 240-252, 262 *seq.*, 270, 273, 296, 321 *seq.*

Ice, constitution of, 98.
Ideal solutions, 166.
Imbibition of gels, 364.
Indicators, theory of, 252-261.
Inelastic collisions between atoms, 462 *seq.*
Inert gas upon (gaseous) equilibrium, effect of a, 145, 146.
Inertia of an atom, 48.
— — — electron, 48.
Influence of solvent upon the solute, 198 *seq.*
Inorganic ferments, 453.
Internal pressure, 78. *See also* Cohesion.
Intrinsic pressure. *See* Internal pressure.
Inversion of cane sugar (sucrose). *See* Cane sugar.
Invertase upon sucrose, action of, 460, 461.
Iodine ion, catalytic effect of, 420.
— vapour, dissociation of, 132, 136 *seq.*, 150.
Ion alcoholates, 435 *seq.*
— catalysis, 204 *seq.*, 415 *seq.*, 418-429, 433-443.
Ion electric charge on the monovalent, 30.
— hydrates, 435 *seq.*
Ionic equilibria in non-aqueous solutions, 274-278.
— product. *See* Solubility product.
— — of water. *See* Water.
— reactions and equilibria. *See* Electrolytic dissociation.
— theory. *See* Electrolytic dissociation.
Ionisation constant. *See* Dilution law of Ostwald.
— — of water. *See* Water.
— of a gas, 50.
Ions, 155 *seq.*, 188 *seq.*
— coagulation of colloids by, 346 *seq.*
— diffusion of, 376-383.
— in colloid stability, function of, 339-342.
— mobility of. *See* Mobility.
— transport number of. *See* Transport number.
— velocity of. *See* Velocity of ions.
Isochore, 69.
Isoelectric point, 345, 346.
Isohydric solutions, 229-234.
Isolated reactions, 383 *seq.*
Isothermals, 61 *seq.*, 67, 73, 74, 87, 89.
Isotonic solutions, 167 *seq.*, 169, 170, 171.

Joule, 55.
Joule's Law, 55.

Kinetic energy, 3.
— — of a molecule, mean, 17 *seq.*, 43.
— theory of gases, 1.
Kinetics in heterogeneous systems, chemical, Chap. X.
— — homogeneous systems, chemical, Chap. IX.
Kohlrausch's law of mobility of ions. *See under* Migration.

Lactase upon milk sugar, action of, 459, 460.
Langmuir's theory of adsorption, and heterogeneous reaction velocity, 461-472.
Lattice, space, 101 *seq.*
Law of mass-action. *See* Mass-action.
— — the rectilinear diameter. *See* Cailletet Mathias' Law.
Life period, average, 51, 52.
Liquefaction of gases, 59 *seq.*
Liquid-liquid heterogeneous equilibria, 294-298.
— systems, reactions in, 156-163.
Liquids, molecular weight of, 96-98.
Lodge's method of determining absolute velocity of ions, 212 *seq.*

Lowering of vapour pressure, freezing-point, molecular, 174-182.

MAGNETIC field upon charged particle, effect of, 33, 35, 48.
Mass action, law of, 117, 119-123, 134 *seq.*, 137 *seq.*, 145-154, 156-163, 186 *seq.*, 220 *seq.*, 224-229, 255, 289, 292 *seq.*, 298-307, 309-325, 383, 406-409, 416, 432, 436 *seq.*, 440 *seq.*, 459, 479.
Maxwell's theorem of distribution of velocities, 2 *seq.*
Mean free path of molecules, 2, 6 *seq.*, 12 *seq.*
Medium, catalytic effect of, 429 *seq.*
Membrane, semi-permeable, 166 *seq.*, 370.
Mercury, vapour pressure of, 93, 94.
Metals, colloidal, 327, 332, 333, 335-342, 345, 348, 350 *seq.*, 368.
Methyl alcohol, molecular weight of, 97.
Methylamine (methylammonium hydroxide), electrolytic dissociation of, 222.
Migration of the ions, Kohlrausch's law of the independent, 191 *seq.*, 193.
Milk sugar, hydrolysis of, 459 *seq.*
Mixed acids, dissociation of, 234-236.
— solvents, reactions in, 433 *seq.*
Mixtures, liquid, 156-163, 184-186.
— of constant boiling-point, 185.
"Mobile equilibrium," principle of, 137, 158.
Mobility and diffusion, 378 *seq.*
— of ions, 191 *seq.*, 193, 209-214, 275.
Molecular association, 96-98.
— attraction, range of, 7 *seq.*
— diameter and radius. *See* Diameter of molecules.
— rotation, 202.
— surface energy, 96.
— velocities in gases, 2, 3, 5, 6.
— volume, 73.
— weight of colloids, 331.
— — — gases, exact, 81.
— — — liquids. *See* Molecular association.
— — — vapours, 96.
Molecules, constitution of. *See* Atom.
— participating in a reaction, methods of finding the number of, 397 *seq.*
— real existence of, 15-29.
"Momentary" state, 147.
Monomolecular reactions, 384-389, 422, 449, 451, 453 *seq.*, 457.
"Moving boundary" method of determining ionic velocity, 213.

NEBULIUM, 47 *seq.*
Negative catalysis in heterogeneous systems, 455, 467 *seq.*
Negative catalysis in homogeneous systems, 430-443.
Neon, formation of, 53.
Nernst's extension of the distribution law. *See* Distribution law.
— theory of heterogeneous reaction, 447 *seq.*
Neutralisation, heat of, 206-208.
Neutral salt action, 423-429.
Nicholson's theory of the atom, 47 *seq.*
Niton. *See* Radium emanation.
Nitrogen, active, 146.
— fixation of. *See* Ammonia, *also* p. 145.
— peroxide, dissociation of, 132, 138.
Non-aqueous solvents, electrochemistry of, 274-281.
Normal substances, 95 *seq.*
Noyes' rule, 218.

OCTAHEDRON, 100.
"Oil drop" method of determining the charge on an electron, 38 *seq.*
— droplets in air, charge on, 38 *seq.*
— — — water, charge on, 334.
— — — — size of, 332.
— films on water, thickness of, 475.
Oils, "drying" of, 456.
— emulsification of. *See* Emulsification.
Opposing reactions. *See* Reversible reactions.
Optical activity of dissolved substances, 202.
— properties of colloidal solutions, 331 *seq.*
— refractivity of dissolved substances, 202.
Order of a reaction, 384 *seq.*, 397-398.
Osmose, electrical. *See* Endosmose.
Osmotic pressure, 164-183.
— — accurate measurement of, 173 *seq.*
— — and lowering of vapour pressure, relation between, 178.
— — of colloidal solutions, 330, 331.

PARTICLES, colloid, oil, etc. *See* Colloidal particles.
Partition coefficient. *See* Distribution coefficient.
Peptisation, 350-353.
Periodic Law, 46.
Perrins' determination of the Avogadro constant, 16.
Phase rule, 288, 290.
Phosphine, decomposition of, 395.
Photo-electric effect, 44, 469.
"Poisoning" the catalyst. *See* Catalytic poisons.

Polymerised substances, 80, 95, 96-98, 180 *seq.*, 200, 292, 294-296.
Potassium chloride, electrolytic dissociation of, 216.
— sulphate, electrolytic dissociation of, 217.
Precipitate formation, 310-325.
Precipitation of colloids. *See* Colloid particles, coagulation.
Preservatives, action of, 478.
Pressure, dissociation. *See* Dissociation pressure.
— exerted by a gas, 4 *seq.*
— internal. *See* Cohesion.
— of saturated vapour. *See* Vapour.
— on dissociation, effect of, 137 *seq.*, 145.
— osmotic. *See* Osmotic pressure.
— partial, 124 *seq.*
Principle of corresponding states. *See* Corresponding states.
"Promoters," 480.
Protective effect. *See* Peptisation.
Protyle, 47.
Pseudo-acids and pseudo-bases, 264.
Pulsating catalysis, 455.

QUADRIMOLECULAR reactions, 393.
Quinquemolecular reactions, 394.

RADIO-ACTIVE change, 50 *seq.*, 387, 388, 404, 440.
Radiometer, the, 15.
Radium emanation, 47, 52, 387, 388.
Radius of a colloid particle, 333.
— — an atom or molecule. *See* Diameter of molecules.
Ramsay-Young boiling-point law, 92.
— — equation, 68-71, 76, 77.
Range of molecular attraction. *See* Molecular attraction.
Rare gases, viscosity and molecular dimensions of the, 12.
Rate of adsorption or condensation, 463 *seq.*
— — reaction, 117 *seq.*, 383 *seq.*, 444 *seq.*
— — — effect of pressure on, 414.
— — — — — temperature on, 409-414, 446, 458, 465 *seq.*
Rays. *See* α, β, γ, rays. *Also* X-rays.
Reactants, 117.
Reactions, heterogeneous, Chap. X.
— in gaseous systems, Chap. III.
Recombination of gaseous ions, 392.
Rectilinear diameter, law of the. *See* Cailletet-Mathias' Law.
Reduced equation of state, 83.
Refractive index of gases, 11.
— — — solutions, 202.
"Relaxation, time of," 462.
Reserve acidity and alkalinity, solutions of, 262-264.
Resultants, 117.
Reversible reactions, Chap. III., 156-163, 220-224, 289, 292-295, 298-325, 406-409, 416, 440 *seq.*, 45[illegible], 479.
Rock salt. *See* Sodium chloride.
Roentgen rays. *See* X-rays.
Rotatory power. *See* Optical activity.

SALT action, neutral. *See under* Neutral.
Salts, electrolytic dissocation of, 197 *seq.*, 215-218, 225 *seq.*
— hydrolysis of. *See* hydrolysis of salts.
— in solution, mixtures of, 205 *seq.*
Saturated layer in heterogeneous reactions, 447, 453.
— vapour, formulæ for pressure of, 92-96.
— — of ammonium chloride. *See* Ammonium chloride.
Semi-permeable membrane. *See* Membrane.
Side reactions, 399 *seq.*
Silver nitrate, electrolytic dissociation of, 217.
Simultaneous reactions, 398 *seq.*
Soap as an emulsifying agent, 353 *seq.*
— detergent action of, 354.
— solutions, constitution of, 349, 350, 370 *seq.*, 372.
— — viscosity of, 370.
Sodium chloride, crystal, structure of, 111.
— — electrolytic dissociation of, 276.
Solid-liquid heterogeneous equilibria, 308-325.
Solubility product, 311-325.
Solution, solid, Chap. VI.
Solutions, liquid, 164 *seq.*
— — diffusion in, 376.
— of electrolytes, Chap. V.
Solvation, 184-186, 277.
Soret phenomenon, 170.
Specific gravity of solutions, 201.
— heat of gases. *See under* Gases.
Spreading of liquids on one another, 476.
State, continuity of. *See* Continuity of state.
— equations of. *See* Characteristic equations.
Stokes' expression for steady motion through a viscous medium, 22, 24, 40 *seq.*, 42, 339.
Strength of acids, comparison of, 237-240.
Strong electrolytes, anomaly of. *See* Anomaly.
Sugar. *See under* Cane sugar, Milk sugar.
Sulphides, solubility of metallic, 317-320.
Sulphur, coagulation of colloidal, 347 *seq.*
Sulphuric acid manufacture. *See* Contact process.
— — on alcohol, action of, 162.

Surface action. *See* Catalysis in heterogeneous systems.
— (capillary) layer, gelatinous, 477.
— — — Langmuir's theory of constitution of the, 461-477.
— concentration, 457.
— energy, molecular, 96 *seq.*, 98.
— tension method of determining molecular weight of liquids, 96 *seq.*
Suspensions, Chap. VIII.
Swelling of gels. *See* Imbibition.

TAUTOMERISM, 254 *seq.*, 264 *seq.*
Technical applications of catalysis, 477-481.
Temperature coefficient of chemical reactions. *See* Rate of reaction.
— — — surface energy, 96.
— definition of, from the kinetic standpoint, 3 *seq.*
Tension, surface, 96.
Termolecular reactions, 392 *seq.*
Tetrahedron, 101.
Thermochemical comparison of strength of acids, 238, 239.
Thomson, Sir J. J., structure of the atom, 33 *seq.*
Thomson's, James, isothermals, 65-68.
Transmutation of the elements, 53.
Transport number of ions, Hittorf's, 209 *seq.*
— — — — true, 213 *seq.*

UNDISSOCIATED molecule, catalytic effect of. *See* Neutral salt action.
Unimolecular. *See* Monomolecular.
Union of ions. *See* Recombination.
Unit of electricity, natural. *See* Electron.
— — matter in crystals, 110.

VAN'T HOFF's theory of osmotic pressure. *Sec under* H.
Vaporisation. *See* Evaporation.
Vapour, constitution of water-, 98.
— pressure (saturated) formulæ, 92 *seq.*
— — density and dissociation of ammonium chloride, 302-307.
Vapour pressure, lowering of. *See* Lowering.
— — of mercury. *See* Mercury.
Vapours, molecular weight of, 96.
Velocities of molecules. *See* Molecular velocities.
Velocity constant. *See* Rate of reaction.
— of ions, absolute, 212.
— — — in an electric field, 212.
— — — methods of measuring, 209-214.
Viscosity and mobility of ions, 275.
— correction for conductivity, 215 *seq.*
— of a colloid in relation to its electric charge, 369.
— — colloidal solutions. *See* Colloidal solutions.
— — gases, 6, 7, 11.
— — and mean free path, 6, 11.
— — soap solutions, 370.
— — solutions, 277.
Volume method of comparing strengths of acids, 239.

WAALS, van der, equation, 71-84.
Washburn's reference substance, method of determining transport number, 213 *seq.*
Water-alcohol mixtures, dissociation of electrolyte in, 277.
— as a negative catalyst, 432, 433, 434, 435 443.
— — — positive catalyst, 302 *seq.*, 414 *seq.*
— — — solute, 278-281.
— constitution of liquid, 98.
— gas reaction, 127, 151.
— ionic product of, 240 *seq.*, 269-274.
— ionisation constant of. *See* Water, ionic product of.
— molecular weight of liquid, 97.
— vapour, dissociation of, 132, 135, 136.
Wegscheider's test for side reactions, 400-402.
von Weimarn's theory of the colloidal state of matter, 328 *seq.*
Wheatstone bridge, 189 *seq.*
Wiedemann-Franz Law, 44.

X-RAYS and crystal structure. *See* Crystal structure.

ZINC-BLENDE, structure of crystal of, 113 *seq.*

AUTHOR INDEX.

Abegg, 190, 213, 224, 225, 233, 307, 322, 454.
Acree, 424, 427, 428.
Aimée, G., 118.
Amadori, 278.
Amagat, 55, 57, 58, 59, 61, 68, 82, 84.
Anderson, 361.
Andrews, 59, 61, 63, 64, 65, 66, 77.
Antropoff, 455.
Appleyard, J. R., 322.
Armstrong, 459, 460.
Arrhenius, 177, 180, 181, 182, 184, 189, 192, 193, 194, 197, 198, 205, 206, 215, 216, 230, 231, 232, 236, 239, 240, 246, 270, 274, 323, 324, 410, 411, 412, 413, 424.
Auerbach, 320.
Aulich, 290.
Avogadro, 5, 17, 55, 165, 171, 172, 174. 177, 179, 182, 194, 195.

von Babo, 175.
Bagster, 281.
Baker, 302, 306.
Balcom, 402.
Baly, E. C. C., 204, 265, 413.
Bancelin, 360.
Bancroft, W. D., 253, 347, 348, 349, 350, 351, 352, 355, 366, 374-5.
Barker, T. V., 99.
Barnes, 68.
Baume, 417.
Bayliss, 331.
Baynes, 78.
Beans, 340, 341.
Beckett, E. G., 260.
Beckmann, 179, 295.
Begeman, 38.
Bennett, 98.
Bergius, 278, 280.
von Berneck, 453, 457.
Berthelot, D., 80, 81.
Berthelot, M., 119, 157, 158, 159, 160, 161, 291, 294, 407, 409.
Berthollet, 118.
Bertrand, 92.
Berzelius, 117.
Bigelow, 430.
Billitzer, 335.
Biltz, 349.
Biot, 92.
Blagden, 179, 180.
Bodenstein, 124, 125, 127, 129, 130, 131, 132, 133, 136, 142, 144, 432, 450, 451, 452, 471, 472, 473.
Bodländer, 345.
Boltzmann, 31, 32.
Bone, 481.
Bonz, 162.
Boyle, 4, 5, 6, 7, 54, 55, 56, 62, 68, 72, 73, 165, 167, 168, 169, 170, 171, 173, 174.
Bradley, L., 373.
Bragg, W. H., 99, 102, 110, 113, 115.
Bragg, W. L., 99, 106, 110, 113, 115.
Bramley, 163.
Braun, 121.
Braune, 433.
Bravais, 101.
Bredig, G., 221, 222, 223, 249, 250, 251, 270, 327, 332, 333, 340, 373, 402, 418, 419, 420, 424, 433, 434, 453, 454, 455, 456, 457, 458.
Briggs, T. R., 355, 357, 358, 359, 366 *seq.*
Brooks (Miss), 449.
Brown, 333.
Bruner, L., 319, 320, 429, 446, 447, 453.
Bruni, 278, 287.
Brunner, E., 447, 459.
de Bruyn, Lobry, 332, 418.
Burke, Miss, 276.
Bunsen, 406.
Burton, E. F., 42, 335, 336, 337, 338, 339, 345, 346, 375.
Butler, 314.
Byk, 1.

Cailletet, 63, 65, 80.
Calvert, 303.
Carrara, 276, 277, 278.
Carrol, 275.
Cash, G., 173.
Caspari, 331.
Centnerszwer, 279.
Charles, 5, 54, 165.
Chwolson, 73.
Clausius, 11, 13, 73, 84, 85, 86, 91, 195.
Clayton, W., 355, 431.
Coehn, 364.
Cohen, 276.
Coleman, 428, 429.
Collie, 49, 53.

Coppet, 179, 180.
Craft, 417.
Cripps, 60.
Cruikshank, 405.
Curtius, 418.
Cuthbertson, 11.

DALTON, 145, 171, 186, 291, 306.
Davies, 282.
Dawson, H. M., 163, 424, 426, 427.
Deacon, 133, 143, 145, 151.
Debray, H., 119.
Denham, 243, 246, 453, 454, 455, 459.
Dennison, 163, 213.
Desch, 287.
Devaux, 475.
Deville, 119.
Dieterici, C., 86, 87, 88, 89, 90, 91.
Diethelm, 454.
Dimroth, 430.
Dixon, 414, 415.
Dolezalek, 127, 163.
Donders, 169.
Donnan, 276, 331, 332, 354, 371, 394, 423.
Dorochewski, 184.
Drucker, 226.
Dumas, 96, 302, 303, 304.
Dutoit, 275.

EASTLACK, 340, 341.
Einstein, 21, 22, 23, 27, 29, 369.
von Ekenstein, 418.
Eötvös, 96, 97, 98.
Esson, 119.
Eykmann, 182.

VON FALCKENSTEIN, 133, 140, 141.
Falk, 215, 216, 416, 417.
Faraday, 188, 457.
Farmer, R. C., 249, 252.
Farrow, 370, 461.
Federlin, 403.
Fick ,376, 377, 380, 444.
Finckh, K., 127.
Findlay, 211, 308, 310.
Fink, C. G., 472.
Fischer, 352.
Fitzgerald, 443.
Fletcher, H., 42.
Flugel, 226.
Fock, 284.
Förster454.
Fourier, 444.
Fraenkel, 249, 419, 433.
Franz, 44.
Frazer, 173.
Freundlich, 343, 351, 365. 366, 369, 373. 375, 457, 460.
Friderich, 275.
Friedel, 417.
Friend, N., 46.
Fulhame, Mrs., 415.

GAUS, 213.
Gay-Lussac, 5, 54, 68, 133, 165, 169, 170, 171, 173.
Geiger, 38, 127.
Getman, 200.
Gibbs, 98, 457, 474.
Goddard, 353.
Godlewski, 276, 414.
Goldschmidt, H., 418, 421, 423, 424, 434, 435, 436, 438, 439, 448.
Goodwin, 316.
Gouy, 16, 17, 22, 333.
Graham, 326, 327, 330.
Gray, 53.
Griffin, 460.
Griffith, R. O., 441.
Groves, 119.
Guldberg, 80, 119, 182.

HABER, F., 93, 127, 128, 133, 138, 142, 144, 456, 479.
von Halban, 430.
Hall, 75.
Hamburger, 169.
Hantzsch, 264, 265, 278.
Harcourt, 119.
Hardy, 335, 340, 342, 345, 346, 347, 348, 373, 476.
Hargreaves, 478.
Harkins, 371, 474.
Harris, 331.
Harrison, W., 369.
Hartley, 417.
Hartung, 163.
Haskell, R., 376, 380, 382.
Hatschek, 362, 368, 369.
von Hauer, 282.
Helmholtz, 98, 334, 336, 338, 339.
Henri, V., 332, 461.
Henry, P., 157.
Henry, W., 172, 289, 292, 293.
Hertz, 92, 93, 465.
Herz, 296.
Herzog, 454.
Hess, 185.
Heydweiller, 270, 271, 274.
Hibbert, 420.
Hittorf, 191, 209, 213, 214, 280.
van't Hoff, 18, 19, 116, 120, 159, 165, 166, 168, 170, 171, 172, 173, 174, 177, 178, 179, 181, 182, 183, 189, 194, 195, 196, 198, 227, 228, 274, 285, 291, 292, 293, 393, 395, 398, 410, 411, 430.

Hoffmann, 96.
Hohmann, 160.
Holborn, 192.
Holland, 173.
Hollemann, 400.
Holt, A., 385.
Horstmann, 182, 301.
Hudson, 270, 272, 273, 460.
Humphrey (Miss), 369.

INGLE, 456.
Isambert, 300, 301.
Ishizaka, 369.

JAHN, H., 226.
Jeans, 1, 11, 13, 15.
Jellinek, 127, 145.
Johnson, F. M. G., 306.
Johonnot, 10.
Jones, H. C., 184, 185, 200, 275, 277, 278.
Jones, W. J., 160, 407, 416.
Joule, 8, 55.
Judson, 393.
Jungfleisch, 294.
Just, 394.

KAHLENBERG, 206, 279, 280.
Kanolt, 270.
Kendall, 212, 219, 221, 228, 417, 426.
Knietsch, 144.
Knight, 75.
Knoblauch, 406, 407.
Knoevenagel, 478.
Knox, 320.
Knudsen, 93, 465.
Koelichen, 416, 418.
Kohlrausch, 185, 189, 191, 192, 193, 194, 200, 204, 209, 211, 212, 215, 219, 228, 250, 270, 271, 277.
Kolhatkar, 418.
König, 395.
Krafft, 372.
Kranendieck, 471.
Kremann, 162.
Krönig, 206.
Krüger, 469.
Kruyt, 361.
Kuenen, 73, 81, 84.
Kulgren, 431.
Kuriloff, 298.
Kurlbaum, 38.

LAMB, 334, 335, 336, 339, 345, 346.
Langevin, 27.
Langmuir, 14, 115, 132, 371, 459, 461, 462, 463, 465, 466, 467, 468, 469, 471, 473, 474, 477.
Lapworth, 160, 407, 416, 424, 432, 443.
Laue, 106.
Le Chatelier, 121, 132, 299.
Leduc, 82.
Lehfeldt, 120.
Lehmann, 282.
Lemoine, 124.
Le Rossignol, 133, 394.
Lewis, G. N., 133, 213, 218, 281.
Lewis, W. C. M., 10, 78, 332, 375, 441.
Ley, 248.
Lichty, 434.
Lindemann, F. A., 44.
Linder, 335, 342, 344, 353, 368.
Lippmann, 10, 336, 373.
Lodge, 188, 212, 213.
Loeb, 206.
Lombard, 303, 304, 305, 306.
Lorentz, 17.
Lottermoser, 350.
Lowenherz, 270.
Löwenstein, 132.
Lunden, 223.
Lunge, 138, 139, 140, 141, 253.
Lummer, 17.
Luther, 394, 431.

McBAIN, 261, 349, 350, 428, 429, 469.
McCourt, 481.
McDougall, F. H., 394.
McGowan, 325.
Mackey, 456.
Makower, 53.
Malaguti, 118.
Manchot, 454.
Marc, R., 449.
Marmier, 138, 139, 140, 141, 253.
Martin, 349, 350.
Masson, J. I. O., 325.
Mathias, 63, 65, 80.
Mayer, 46.
Maxwell, J. Clerk, 2, 11, 13, 462.
Meldrum, 199.
Mellor, 116, 132, 157, 395, 398, 404, 418.
Mendeleef, 46, 184.
Menschutkin, 429.
Menzies, 93, 177.
Merton, 203.
Meyer, L., 46.
Meyer, O. E., 1.
Meyer, Victor, 96, 132, 136, 302, 303, 304.
von Meyer, 350.
Millar, 433, 434.
Miller, Lash, 213.
Millikan, 15, 21, 37, 38, 39, 40, 41, 42, 43.
Moore, B., 331.
Morse, 173, 174.
Morton, W. B., 35.
Moseley, 115.
Mosotti, 11.
Mukherjee, 361.
Müller, 375.
Myers, C. N., 173.

NAGEL, 352.
Natanson, E. and L., 132
Nelson, J. M., 416, 417, 460.
Nernst, 3, 44, 93, 127, 132, 136, 145, 160, 181, 186, 199, 270, 274, 278, 288, 290, 291, 292, 295, 296, 297, 312, 315, 322, 373, 376, 382, 429, 445, 447.
Newton, 10.
Nicholson, 47, 48, 49, 50, 53.
Nollet, 164.
Noyes, A. A., 215, 216, 218, 225, 270, 281, 322, 323, 378, 393, 444, 445, 447.

OBERBECK, 14.
Oberer, 454.
Oden, 347.
Oesper, 354.
Ohlmer, 471, 473.
Ohm, 188, 193.
Öholm, 381, 382.
Onnes, 79, 95.
van Oordt, 133.
Orton, 385.
Osaka, 272, 273.
Ostwald, Wm., 119, 190, 203, 204, 220, 221, 223, 226, 227, 229, 235, 238, 239, 241, 242, 254, 255, 256, 265, 267, 269, 270, 276, 280, 312, 323, 325, 398, 431, 440, 441, 480.
Ostwald, Wo., 375.
Oudemann, 202, 203, 209.

PAAL, 350, 351.
Palmaer, 205, 427.
Pamfil, 417.
Papaconstantinou, 361.
Parrot, 164.
Partington, 228, 229.
Patterson, 49, 53, 60, 79.
Paul, 206.
Peddle, 200.
Perman, 32, 282.
Perrin, 11, 16, 17, 18, 19, 21, 22, 23, 24, 27, 29, 38, 41, 42, 333, 366, 374.
Pfeffer, 19, 164, 165, 167, 169, 170, 172.
Pickering, 354, 356.
Picton, 335, 342, 344, 353, 359.
Planck, 17, 38.
Pockels, 333.
Pohl, 133.
Porter, A. W., 92, 432.
Powis, 340, 346, 373.
Poynting, 10.
Preuner, G., 132.
Pribram, 364.
Price, 403.
Pringsheim, 17.

QUINCKE, 9, 10, 334, 354.

RAMSAY, Sir William, 16, 32, 47, 53, 68, 69, 70, 71, 76, 77, 91, 92, 96, 97, 98, 278, 333, 342, 388.
Ramsden, 354, 356-360.
Ramstedt (Miss), 427.
Rankine, A. O., 11, 12.
Rankine, W. J., 92.
Raoult, 175, 176, 177, 179, 180, 181, 182, 196, 197.
Raveau, 84.
Rayleigh, Lord, 14, 475.
Regener, 38.
Reinold, 10.
Rice, F. O., 413.
Richardson, O. W., 44, 132.
Ritzel, A., 449.
Roaf, 331.
Robinson, 478.
Roon, 354.
Rosanoff, 440, 441.
Roscoe, 185, 186, 406.
Rose-Innes, 32.
Roshdestwenski, 184.
Rothmund, 325.
Rücker, 10.
Rudolphi, 227, 228, 276.
Rüdorff, 179, 180.
Rudorff, G., 60.
Rümelin, 388.
Rutherford, 38, 45, 52, 53, 386, 387, 388, 392, 404, 405, 449.

SACERDOTE, 82.
St. Gilles, 119, 157, 158, 159, 160, 161, 409.
Sandqvist, 352.
Scheffer, 307.
Schidlov, 42.
Schlundt, 279.
Schulze, 342, 346, 347, 348.
Senter, 424, 432, 433, 453, 459.
Sherrill, 323.
Shields, 96, 97, 98, 245, 270, 273, 278.
Siedentopf, 331.
Skraup, 401.
Slade, 352.
Smiles, 417.
Smith, A., 93, 303, 304, 305, 306.
Smith, S. W. J., 210.
von Smoluchowski, 29, 360, 364, 369.
Snethlage, 424, 433.
Soddy, 51, 53, 386, 387, 388, 404, 405.
Soret, 170.
Spencer, 454.
Speranski, 282.
Spitalsky, 419.
Spohr, 411.
Starck, 132, 136.
Steele, 213, 281.
Stern, 420.

Stieglitz, 323, 325.
Stokes 21, 24, 25, 36, 40, 335, 339, 345.
Strutt, 146.
Sutherland, 9, 12, 15.
Svedberg, T., 29, 327, 374.

Targe, 469.
Tammann, 73, 170, 171, 173, 175.
Taylor, H. S., 424, 425, 427.
Taylor, W. W., 375.
Teletow, 453, 454, 458.
Thomsen, 238.
Thomson, Sir J. J., 10, 21, 33, 35, 44, 45, 47, 48, 199, 274, 278, 333, 429, 457.
Thomson, James, 65, 66, 67, 73, 87, 88.
Thomson, Sir William (Lord Kelvin), 8, 14, 177, 330.
Thorne, 369.
Titoff, 431.
Tizard, 247, 256.
Tolloczko, 446, 447.
Tolman, 208.
Töpler, 170.
Townshend, 42, 50, 392.
Traube, 164.
Trautz, 448.
Trimble, 478.
Turner, W. E. S., 98, 199, 200.
Tutton, 99.
Tyndall, 326, 331.

Udby, 435, 436.
Ulzer, F., 374.

Valson, 202.
Vanstone, E., 283.
Vosburgh, 460.
de Vries, 167, 173.

Waage, 119.
van der Waals, J. D., 8, 9, 12, 13, 57, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 84, 85, 86, 87, 89, 91, 92, 93, 97.
Waddell, J., 157, 253.
Wakeman, 276.
Walden, P., 60, 199, 275, 278, 279, 280.
Walker, J., 129, 223, 246, 252, 265, 269, 270, 280, 322, 393, 419.
Walton, 420.
Warder, 391, 411.
von Wartenberg, 132.
Washburn, 213, 215, 226, 239, 262, 264.
Wason, 393.
Wedekind, 448.
Wegscheider, 307, 400, 401, 402.
von Weimarn, 328, 330, 344, 352.
Westgren, 42.
Wheatstone, 189.
Whetham, 213, 343, 344.
Whitney, 364, 445, 447.
Whytlaw-Gray, 60, 79.
Wiedemann, 44.
Wiener, 14.
Wijs, 270, 271, 415.
Wilderman, 276, 448.
Wilhelmy, 117, 118.
Will, 418.
Williams, P. H., 100.
Wilson, C. T. R., 35, 38.
Wilson, H. A., 35, 36.
Wislicenus, 265.
Wöhler, 456.
Wood, R. W., 47.
Woudstra, 371.
Wüllner, 175.

Young, S., 60, 63, 65, 68, 69, 70, 71, 76, 77, 79, 83, 84, 91, 92.
Young, S. W., 353.

Zaitschek, 162.
Zawadzki, 319.
Zinn, J. B., 173.
Zsigmondy, 331, 350, 361, 375.

STATE CENTRAL LIBRARY VIP Road Kolkata

117A

PRINTED IN GREAT BRITAIN BY THE UNIVERSITY PRESS, ABERDEEN